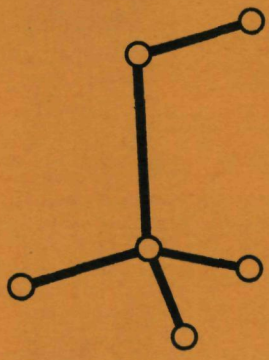

HYPERFINE STRUCTURE IN INTERNAL ROTOR MOLECULES

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HYPERFINE STRUCTURE

IN INTERNAL ROTOR MOLECULES

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PROEFSCHRIFT

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Aan mijn ouders

Aan Elly

CONTENTS

CHAPTER 1

INTRODUCTION

I. INTRODUCTION.

Hindered internal motion in molecules has been a subject of interest for long times. Molecules in which this type of motion occurs consist of two or more groups of nuclei which can move with respect to each other. The internal motion is generally not free, but hindered by potential barriers. The type and strength of these barriers determine the character of the internal motion. For high barriers the motion is a libration, because the probability to penetrate a barrier is small. The motion is an almost free rotation in the case of very low barriers. It is customary to call both types of internal motion "rotation", a custom which we shall observe in the following.

A considerable amount of information about the gross features of the internal rotation was and is being obtained from the rotational spectra in the microwave region. From the nature of the microwave spectrum (strength and separation of librational satellite lines, splitting of the rotational lines of symmetric and asymmetric type of rotors) the height and shape of the potential barriers can be determined in a semi-empirical way. The origin of the potential barrier is, however, not well understood. They are apparently caused by the interactions of two groups of nuclei and electrons.

It is well known that the hyperfine structure and the related

molecular quantities are a very important source of information about the electronic structure and interactions in molecules. The present investigation was intended primarily to investigate the hyperfine structure of molecules with hindered internal rotation, both from theoretical as from experimental side. The goal is to examine how internal rotation influences the well known hyperfine interactions in rigid rotor molecules. The results might also be useful in the future for a better understanding of the phenomenon of internal rotation and in particular of the origin of the hindering potential barrier in terms of electronic structure.

All microwave spectra of internal rotors until the start of the present investigation were obtained at a rather low resolution and no information could be acquired about the hyperfine interactions in these molecules. Moreover, no theory was available that could be used as a basis for the interpretation of hyperfine spectra. Only recently Radford (1) reported the measurement of the $(J,K,\tau\pm) = (1,1,3+) \rightarrow (1,1,3-)$ transition of methanol (CH_3OH) at 835 MHz in a high resolution experiment. He did resolve the hyperfine structure, but made no attempt to analyse it.

The subject of the present investigations was also the methanol molecule. We have choosen this molecule because it is one of the most intensively investigated internal rotors and, moreover, it is with the exception of hydrogen peroxide (H_2O_2) also the simplest one. Many transitions of CH_3OH have been reported in the centimeter and millimeter region, and most of them are well identified. The barrier height and internal rotation wavefunctions have been calculated from these spectra. An additional importance of our

investigation stems from the recent discovery of methanol emission in the direction of the galactic center (2). This emission originates from transitions which were also subject of the present investigation. The hyperfine structure of these transitions is very important for the determination of the line shape and so called rest frequencies of the galactic emission lines.

II. HYPERFINE STRUCTURE OF ROTATIONAL SPECTRA.

In the absence of external electric and magnetic fields the main contribution of the hyperfine structure in rotational spectra originates in:

1) nuclear quadrupole interactions,
2) spin-rotation interactions, and
3) nuclear spin-spin interactions.

The first interaction arises from the coupling between the nuclear electric quadrupole moment with the gradient of the electric field at a given nucleus. The interaction is absent in $^{12}CH_3OH$ since this molecule contains only nuclei with spin 0 or $\frac{1}{2}$. The deuterated species of methanol (CH_3OD, CD_3OH, CD_3OD) were beyond the scope of the present investigation.

The nuclear spin-rotation interaction originates in the interactions of nuclear magnetic dipole moments with the effective magnetic field at the nucleus. This magnetic field is produced by the rotation of the nuclear frame and by the excitation of electrons into higher electronic states with non-zero angular momentum by the coupling between electronic motion and molecular rotation. The rotation has to be considered as composed of the overall-rotation of

the molecule and the internal rotation. So there are two contributions to the spin-rotation interaction, namely the spin-overall rotation and the spin-internal rotation interaction. The strength of the spin-rotation interaction cannot be calculated in advance, but is expected to be of the order of 10 kHz, as it is in rigid rotor molecules.

The nuclear spin-spin interaction is the interaction between magnetic moments associated with nuclear spins. It consists theoretically of two parts: the direct- and the indirect, or electron-coupled spin-spin interaction. The latter interaction is very weak (< 1 kHz) and will be neglected in the following. The magnitude of the former interaction depends on the internuclear distances, which are not constant due to the internal rotation. The strength of this interaction can be calculated from the geometry of the molecule and the known internal rotation wavefunctions. For CH_3OH it is of the order of 10 kHz.

At the start of the present investigation no theory of the hyperfine structure in internal rotor molecules was available. In Sect.2-I a Hamiltonian including hyperfine interactions is derived. This Hamiltonian is applicable not only to the methanol molecule, but also to other internal rotor molecules with only one internal degree of freedom. The last restriction is not essential and the hyperfine Hamiltonian is easily extended to molecules with more internal degrees of freedom. In the remaining part of Chap.2 the structure of the hyperfine energy matrix and explicit expressions for the matrix elements and hyperfine coupling constants are introduced for methanol-like molecules.

III. THE EXPERIMENTAL METHOD.

Rotational transitions of methanol cover a large frequency region, from a few hundreds of MegaHertz into the submillimeter region. The for the investigation most relevant transitions lie in the microwave region (1-50 GHz).

The resolving power of a conventional microwave absorption spectrometer is generally insufficient at frequencies higher than a few GigaHertz, because of the Doppler broadening of the lines. This broadening is considerably reduced in spectrometers using molecular beams. The ultimate resolution of such spectrometers is determined by the uncertainty principle of Heisenberg, if all broadening due to the Doppler effect and other instrumental effects is eliminated. The half-width (at half of the maximum intensity) of the line, $\Delta\nu$, due to the Heisenberg broadening in beam-spectrometers is given by:

$$\Delta\nu \simeq \frac{\bar{v}}{2L} \quad ,$$

where $\bar{v}$ is the most probable velocity of the molecules in the beam and L is the length of the molecular path through the radiation field.

For the investigation of rotational transitions two types of beam-spectrometers enter into consideration

1) Beam-Absorption Spectrometer (BAS), and

2) Beam-Maser Spectrometer (BMS).

In the BAS the Doppler broadening is considerably reduced by sending a molecular beam perpendicular to the direction of propagation of the microwave radiation. In a practical realization of

this principle a molecular beam is sent through the region between two plates of a parallel plate type absorption cell (Fig.3 Chap.3). A diaphragm at liquid nitrogen temperature serves to trap the molecules not travelling in the proper direction. Information about the molecular energy levels is obtained from the measurement of the power absorbed by the molecules in the beam. The sensitivity of a BAS is proportional to the square of the frequency and becomes a serious problem below about 40 GHz. In this frequency region a BMS is an obvious choice for high resolution spectroscopy. In a BMS a considerable gain in sensitivity with respect to a BAS may be obtained by application of the maser principle introduced by Gordon et al (3). Doppler broadening is eliminated by sending a molecular beam through a resonant structure (cavity or interferometer). However, a BMS equiped with a cylindrical microwave cavity cannot be used for frequencies above 30-40 GHz, since the dimensions of such cavities become too small for transmission of strong molecular beams. Although beam-maser spectrometers have been operated at frequencies as high as 200 GHz using interferometers instead of conventional cavities, resolution is limited by the rather narrow width (<10 cm) of radiation distribution. With cylindrical cavities, lengths of 30 cm at 30 GHz to 1 m at a few GHz can be used, yielding half-widths of 300 - 1000 Hz.

The operation of the BMS is based on the phenomenon of stimulated emission of the molecules in the beam. The molecular beam passes through a state selector before entering the microwave cavity (Fig.1 Chap.3). The state selector consists usually of an electrostatic octupole which exerts a force on a molecule in the beam.

The force depends on the Stark energy of the specific molecular state. All molecules in the lower of the two states involved in the transition are normally removed from the beam, while molecules in the upper state are deflected to the central axis of the state selector and enter the cavity. In the ideal situation, the molecules entering the cavity are all in the upper state from which they are stimulated to emit coherently by the electromagnetic field in the cavity.

The power ΔP, emitted by the beam in the BMS or absorbed in the BAS, is proportional to:

$$\Delta P \sim (n_1 - n_2)\, h\nu\, P_{12} \quad ,$$

where n_1 and n_2 are the number of molecules in the upper and lower state, respectively, P_{12} is the transition probability between the two states, and ν is the transition frequency. In the beam-maser spectrometer $n_2 \approx 0$ because of the state selection and hence:

$$\Delta P \sim n_1\, h\nu\, P_{12} \quad .$$

If no state selection is employed, as in the BAS, the difference $n_1 - n_2$ can be approximated by:

$$n_1 - n_2 \approx - n_1 \left(\frac{h\nu}{kT}\right) \quad ,$$

and hence:

$$\Delta P \sim n_1 \frac{h^2\nu^2}{kT} P_{12} \quad .$$

The gain in sensitivity due to the state selection is therefore about $(kT/h\nu)$, which is in the order of 300 for ν = 20 GHz and $T = 300\ ^0K$. It depends, of course, on the Stark effect of the in-

volved molecular states.

The BMS is extremely small banded, and therefore the frequencies of the rotational transitions have to be known with an accuracy of about 200 kHz, before investigation with the BMS is possible. Therefore we first have determined accurately the frequencies of the rotational transitions we intended to investigate (4) These measurements were carried out with a conventional absorption spectrometer with Stark modulation. At the same time the Stark effect of the transition was determined, as it is important for the prospects of efficient state selection. In this way we discovered, for example, that the $(J,K,\tau\pm) = (5,1,3-) \rightarrow (5,1,3+)$ transition of methanol, which we intended to investigate, is completely unsuitable for beam-maser spectroscopy because state selection is impossible. The Stark effect of the rotational levels was also calculated and the agreement with the measurements was satisfying (5).

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CHAPTER 2

THEORY

I. THE HAMILTONIAN.

The Hamiltonian of a $^1\Sigma$ molecule with internal rotation can be written as: $H = H_R + H_{HF}$, where H_R is the Hamiltonian of the overall rotation of the molecule and H_{HF} represents contributions to the energy because of hyperfine interactions originating in the spins of molecular nuclei (spin-spin, spin-rotation, spin-internal rotation). We restrict ourselves in this Section to internal rotor molecules with only one internal degree of freedom (CH_3OH and H_2O_2 for example). If we choose a molecule-fixed system of reference *) (x,y,z, not necessarily the principal-axis system) with the origin in the center of mass, the overall velocity of a nucleus K is given by:

$$\dot{\bar{r}}_K = (\bar{\omega} \times \bar{r}_K) + \bar{v}_K \ . \qquad (1)$$

Herein $\bar{r}_K$ is the radius vector of the K-th nucleus, $\bar{v}_K$ is the velocity of this nucleus relative to the molecule-fixed system, and $\bar{\omega}$ is the overall angular velocity of the molecule-fixed system relative to the space-fixed system. In internal rotor molecules with one internal degree of freedom, the velocity $\bar{v}_K$ of all nuclei is perpendicular to a certain axis $\bar{\lambda}$ through the CM and proportional to $\frac{\partial \alpha}{\partial t}$, α being the angle of internal rotation. In this case, for each nucleus K a vector $\bar{\sigma}_K$ can be found such that:

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*) We suppose that such a system can always be defined.

$$\bar{v}_K = - \dot{\alpha}(\bar{\lambda} \times \bar{\sigma}_K) = - \dot{\bar{\alpha}} \times \bar{\sigma}_K \quad , \tag{2}$$

where $\dot{\bar{\alpha}} = \dot{\alpha}\bar{\lambda}$. The sign in the above expression is arbitrary, and depends on the definition of α, $\bar{\lambda}$ and $\bar{\sigma}_K$. Equation (1) can be rewritten as:

$$\dot{\bar{r}}_K = (\bar{\omega} \times \bar{r}_K) - (\dot{\bar{\alpha}} \times \bar{\sigma}_K) \quad . \tag{1a}$$

A. THE HAMILTONIAN EXCLUDING HYPERFINE INTERACTIONS.

The kinetic energy is given by:

$$T = \sum_K \tfrac{1}{2} m_K |\dot{\bar{r}}_K|^2 = \sum_K \tfrac{1}{2} m_K |(\bar{\omega} \times \bar{r}_K) - (\dot{\bar{\alpha}} \times \bar{\sigma}_K)|^2$$

$$= \tfrac{1}{2} \bar{\omega} \cdot \bar{\bar{I}}^{rr} \cdot \bar{\omega} - \bar{\omega} \cdot \bar{\bar{I}}^{\sigma r} \cdot \dot{\bar{\alpha}} + \tfrac{1}{2} \dot{\bar{\alpha}} \cdot \bar{\bar{I}}^{\sigma\sigma} \cdot \dot{\bar{\alpha}} \quad , \tag{3}$$

where the components $I^{ab}_{gg'}$, of the inertia tensors $\bar{\bar{I}}^{rr}$, $\bar{\bar{I}}^{\sigma r}$, $\bar{\bar{I}}^{\sigma\sigma}$ defined with respect to the molecular axes system (g,g'), are defined by:

$$I^{ab}_{gg'} = \sum_K m_K \left[(\bar{a}_K \cdot \bar{b}_K)\, \delta(g,g') - (\bar{a}_K)_g (\bar{b}_K)_{g'} \right] \quad . \tag{4}$$

$\bar{\bar{I}}^{rr}$ is the inertia tensor of the whole molecule and $\bar{\bar{I}}^{\sigma\sigma}$ is sometimes the inertia tensor of one part of the molecule (CH_3OH).

The Cartesian components of the total angular momentum $\bar{R}$ and the angular momentum P conjugate to the angle α of internal rotation are:

$$R_g \equiv \frac{\partial T}{\partial \omega_g} \quad \text{or} \quad \bar{R} = \bar{\bar{I}}^{rr} \cdot \bar{\omega} - \dot{\alpha}\, \bar{\bar{I}}^{\sigma r} \cdot \bar{\lambda} \ ,$$

$$P \equiv \frac{\partial T}{\partial \dot{\alpha}} \quad \text{or} \quad P = - \bar{\omega} \cdot \bar{\bar{I}}^{\sigma r} \cdot \bar{\lambda} + \dot{\alpha} \bar{\lambda} \cdot \bar{\bar{I}}^{\sigma\sigma} \cdot \bar{\lambda} \ .$$

By expressing the angular velocities $\dot{\alpha}$ and $\bar{\omega}$ in terms of the angu-

lar momenta we get:

$$\dot{\alpha} = 2F(\Pi + P) \ , \tag{5}$$

$$\bar{\omega} = 2\,\bar{\bar{A}}\,\bar{R} + 2F(\Pi + P)\,\bar{\rho} \ , \tag{6}$$

where:

$$\bar{\bar{A}} = \tfrac{1}{2}\,(\bar{\bar{I}}^{rr})^{-1} \ ,$$

$$\bar{\rho} = 2\,\bar{\bar{A}}\cdot\bar{\bar{I}}^{\sigma r}\cdot\bar{\lambda} \ ,$$

$$\Pi = (\bar{\rho}\cdot\bar{R}) \ ,$$

$$F = \tfrac{1}{2}\left[\bar{\lambda}\cdot\bar{\bar{I}}^{\sigma\sigma}\cdot\bar{\lambda} - \bar{\rho}\cdot\bar{\bar{I}}^{rr}\cdot\bar{\rho}\right]^{-1} \ .$$

From Eqs.(5), (6) and Eq.(3) follows:

$$T = \bar{R}\cdot\bar{\bar{A}}\cdot\bar{R} + F(\Pi + P)^2 \ . \tag{7}$$

The internal rotation is in general not free, but hindered by the interactions between the atoms of the molecule. We suppose that these interactions can be described by a potential $V(\alpha)$, depending on the internal angle α. The Hamiltonian H_R of the overall- and internal rotation is then:

$$H_R = \bar{R}\cdot\bar{\bar{A}}\cdot\bar{R} + F(\Pi + P)^2 + V(\alpha) \ . \tag{8}$$

The angular momenta $\bar{R}$ and P are associated with rotation of the nuclei alone. The total angular momentum $\bar{J}$ of the molecule, excluding nuclear spins is:

$$\bar{J} = \bar{R} + \bar{L} \ ,$$

where $\bar{L}$ is the angular momentum of the electrons. The latter momentum is zero in first order for $^1\Sigma$ molecules, but not in second

order. Similarly:

$$p = P + L_\alpha \ ,$$

where p is the total angular momentum associated with internal rotation, and L_α the electronic contribution to it.

The rotational Hamiltonian in terms of the total and electronic angular momenta can be written in the form:

$$H_R = (\bar{J} - \bar{L})\cdot\bar{\bar{A}}\cdot(\bar{J} - \bar{L}) + F(\Gamma - \Lambda + p - L_\alpha)^2 + V(\alpha) \ , \qquad (9)$$

with: $$\Gamma = (\bar{\rho}\cdot\bar{J}) \ , \qquad (10a)$$

and: $$\Lambda = (\bar{\rho}\cdot\bar{L}) \ . \qquad (10b)$$

The Hamiltonian (Eq.(9)) can be written as a sum:

$$H_R = H_0 + H_1 \ ,$$

where:

$$H_0 = \bar{J}\cdot\bar{\bar{A}}\cdot\bar{J} + F(\Gamma + p)^2 + V(\alpha) \qquad (11a)$$

is the zeroth order contribution, which is independent of the electronic angular momenta, and

$$H_1 = -2\ \bar{L}\cdot\bar{\bar{A}}\cdot\bar{J} + (\Gamma + p)\xi \qquad (11b)$$

with:

$$\xi = -2\ F(\Lambda + L_\alpha) \ ,$$

is the first order contribution, containing only terms linear in the electronic orbital angular momenta $\bar{L}$ and L_α. The terms quadratic in $\bar{L}$ and L_α can be neglected, because they are independent of the rotational quantum numbers.

B. THE HAMILTONIAN INCLUDING HYPERFINE INTERACTIONS.

In the absence of external magnetic fields the magnetic hyperfine structure originates in interactions (1) between the magnetic moments of the nuclei, and (2) between the nuclear magnetic moments and the magnetic field produced at their positions by the motion of molecular electrons and nuclei. The first interaction is the familiar spin-spin interaction described by a Hamiltonian H_{SS}. The electronic (e) and nuclear (n) contribution to the second interaction, the spin-rotation interaction, is described by the Hamiltonian $H_{SR}^{(e)}$ and $H_{SR}^{(n)}$, respectively. The total hyperfine Hamiltonian is:

$$H_{HF} = H_{SR}^{(e)} + H_{SR}^{(n)} + H_{SS} \ . \tag{12}$$

The "classical" expressions (in MKS-units) for the individual Hamiltonians are (1, 2, 3, 4):

$$H_{SR}^{(e)} = \frac{e\mu_0\mu_N}{4\pi} \sum_i \sum_K g_K \, r_{iK}^{-3} \left[\bar{r}_{iK} \times (\bar{v}_i - \gamma_K \bar{v}_K)\right] \cdot \bar{I}_K \ , \tag{12a}$$

$$H_{SR}^{(n)} = \frac{-e\mu_0\mu_N}{4\pi} \sum_K \sum_{L \neq K} Z_L g_K \, r_{LK}^{-3} \left[\bar{r}_{LK} \times (\bar{v}_L - \gamma_K \bar{v}_K)\right] \cdot \bar{I}_K \ , \tag{12b}$$

$$H_{SS} = \frac{\mu_0 \mu_N^2}{4\pi} \sum_K \sum_{L<K} g_L g_K \, r_{LK}^{-3} \left[(\bar{I}_L \cdot \bar{I}_K) - 3r_{LK}^{-2} (\bar{I}_K \cdot \bar{r}_{LK})(\bar{I}_L \cdot \bar{r}_{LK})\right] \tag{12c}$$

In these expressions $\bar{r}_s$ and $\bar{v}_s$ denotes the radius- and velocity vector, respectively, of particle s (i for electrons, K and L for nuclei) relative to the molecular center of mass, which is assumed to be the center of mass (CM) of all nuclei, $\bar{r}_{iK} = \bar{r}_i - \bar{r}_K$ and $\bar{r}_{LK} = \bar{r}_L - \bar{r}_K$, $r_{iK} = \left|\bar{r}_{iK}\right|$ and $r_{LK} = \left|\bar{r}_{LK}\right|$. The nucleus K is supposed to have mass M_K , charge $Z_K e$ (e positive), spin $\bar{I}_K$, and

nuclear magnetic moment $g_K \mu_N \bar{I}_K$, with g_K the nuclear g-factor and μ_N the nuclear magneton. The Thomass precession factor is given by:

$$\gamma_K = - \frac{Z_K M_p}{g_K M_K} ,$$

with M_p the proton mass.

The Hamiltonians H_{SS} , $H_{SR}^{(e)}$ and $H_{SR}^{(n)}$ can be expressed as products of tensors of rank 1 and 2.

(i) Spin-spin interaction.

This case is formally identical to that of a rigid rotator without internal rotation. The reason is that interaction between nuclear spins is independent of velocities of the nuclei and depends only on their positions. So we have:

$$H_{SS} = \sum_K \sum_{L<K} \bar{I}_K \cdot \bar{\bar{D}}_{KL} \cdot \bar{I}_L , \qquad (13)$$

with:

$$(D_{KL})_{gg'} = \frac{\mu_0 \mu_N^2}{4\pi} g_K g_L r_{KL}^{-5} \left[r_{KL}^2 \delta(g,g') - 3(\bar{r}_{KL})_g (\bar{r}_{KL})_{g'} \right] . \qquad (13a)$$

The angle α will enter into the calculation through the relative positions of the nuclei.

(ii) Spin-rotation interaction.

By substituting the expression for $\bar{v}_K$ given in Eq.(1) into Eq.(12b) we obtain:

$$H_{SR}^{(n)} = \frac{-e\mu_0 \mu_N}{4\pi} \sum_K \sum_{L \neq K} Z_L g_K r_{LK}^{-3} \{ \bar{r}_{LK} \times [(\bar{\omega}_L \times \bar{Z}_{LK}) - (\dot{\bar{\alpha}} \times \bar{\Sigma}_{LK})] \} \cdot \bar{I}_K , \qquad (14)$$

with:

$$\bar{Z}_{LK} = \bar{r}_L - \gamma_K \bar{r}_K \ ,$$

$$\bar{\Sigma}_{LK} = \bar{\sigma}_L - \gamma_K \bar{\sigma}_K \ . \qquad (14b)$$

Since we are dealing with $^1\Sigma$ molecules, we approximate (in first order) the expressions for $\bar{\omega}$ and $\dot{\bar{\alpha}}$ given in Eqs.(5) and (6) by:

$$\bar{\omega} = 2\,\bar{\bar{A}}\,\bar{J} + 2F(\Gamma + p)\,\bar{\rho} \ ,$$

$$\dot{\bar{\alpha}} = 2F(\Gamma + p)\,\bar{\lambda} \ . \qquad (15)$$

With this approximation Eq.(14) reduces to:

$$H_{SR}^{(n)} = \frac{-e\mu_0\mu_N}{2\pi} \sum_K \sum_{L\neq K} Z_L g_K r_{LK}^{-3} \{\bar{r}_{LK} \times [(\bar{\bar{A}}\,\bar{J}) \times \bar{Z}_{LK}] + \\ + (\Gamma + p)\,\bar{d}^n_{LK}\}\cdot\bar{I}_K \ , \qquad (16)$$

with:

$$\bar{d}^n_{LK} = F\{\bar{r}_{LK} \times [(\bar{\rho} \times \bar{Z}_{LK}) - (\bar{\lambda} \times \bar{\Sigma}_{LK})]\} \ , \qquad (16a)$$

or:

$$H_{SR}^{(n)} = \sum_K \{\bar{I}_K \cdot \bar{\bar{N}}^n_K \cdot \bar{J} + (\Gamma + p)(\bar{I}_K \cdot \bar{d}^n{}_K)\} \ , \qquad (17)$$

with:

$$(N^n_K)_{gg'} = \frac{-e\mu_0\mu_N}{2\pi} g_K \sum_{L\neq K} Z_L r_{KL}^{-3} \sum_{g''} A_{g'g''}\{(\bar{r}_{LK}\cdot\bar{Z}_{LK})\delta(g,g'') - \\ - (\bar{Z}_{LK})_g(\bar{r}_{LK})_{g''}\} \ , \qquad (17a)$$

$$\bar{d}^n_K = \frac{-e\mu_0\mu_N}{2\pi} g_K \sum_{L\neq K} r_{KL}^{-3}\,\bar{d}^n_{LK} \ . \qquad (17b)$$

By combining Eqs.(11),(12),(13) and (16) we obtain:

$$H = h_0 + h_1 + h_2 \ ,$$

with:

$$h_0 = H_0 = \bar{J}\cdot\bar{\bar{A}}\cdot\bar{J} + F(\Gamma + p)^2 + V(\alpha) \ , \tag{18a}$$

$$h_1 = H_{SR}^{(n)} + H_{SS} =$$

$$= \sum_K \{\bar{I}_K\cdot\bar{\bar{N}}_K^n\cdot\bar{J} + (\Gamma + p)(\bar{I}_K\cdot\bar{d}_K^n) + \sum_{L>K} \bar{I}_K\cdot\bar{D}_{KL}\cdot\bar{I}_L\} \ , \tag{18b}$$

$$h_2 = H_1 + H_{SR}^{(e)} =$$

$$= -2\ \bar{L}\cdot\bar{\bar{A}}\cdot\bar{J} + (\Gamma + p)\xi + \frac{e\mu_0\mu_N}{4\pi} \sum_i \sum_K g_K r_{iK}^{-3} [\bar{r}_{iK} \times (\bar{v}_i - \gamma_K v_K)]\cdot\bar{I}_K \ . \tag{18c}$$

Herein h_0 represents the unperturbed Hamiltonian and h_1 terms of the perturbed Hamiltonian, which are diagonal with respect to the electronic state; h_2 contains also terms which are off-diagonal in the electronic states.

We perform now a perturbation calculation on h_2 up to second order with respect to the electronic state. The general formula is:

$$\langle h_2\rangle = \langle 0|h_2|0\rangle + \sum_n{}' \langle 0|h_2|n\rangle\langle n|h_2|0\rangle\ (E_0 - E_n)^{-1} \tag{19}$$

where $|0\rangle$ is the ground electronic state with energy E_0 , and $|n\rangle$ the n-th excited state with energy E_n .

(a) First order.

For a $^1\Sigma$ molecule $\langle 0|H_1|0\rangle = 0$ and consequently:

$$\langle 0|h_2|0\rangle = \langle 0|H_{SR}^{(e)}|0\rangle =$$

$$= \langle 0|\ \frac{e\mu_0\mu_N}{4\pi} \sum_i \sum_K g_K r_{iK}^{-3} \{\bar{r}_{iK} \times (\bar{v}_i - \gamma_K\bar{v}_K)\}\cdot\bar{I}_K\ |0\rangle$$

If we approximate $\langle 0\ |r_{iK}^{-3}\ (\bar{r}_{iK} \times \bar{v}_i)|0\rangle$ by $\langle 0|r_{iK}^{-3}|0\rangle\langle 0|\bar{r}_{iK} \times \bar{v}_i|0\rangle$

then this term is zero for $^1\Sigma$ molecules. For $\bar{v}_K$ we use again Eq.(2) and $\langle 0|h_2|0\rangle$ simplifies to:

$$\langle 0|h_2|0\rangle = \frac{-e\mu_0\mu_N}{4\pi} \langle 0|\sum_i \sum_K \gamma_K g_K r_{iK}^{-3} \{\bar{r}_{iK} \times [(\bar{\omega} \times \bar{r}_K) - (\dot{\bar{\alpha}} \times \bar{\sigma}_K)]\}\cdot\bar{I}_K|0\rangle$$

By substituting herein Eq.(16) we get:

$$\langle 0|h_2|0\rangle = \sum_K \bar{I}_K\cdot\bar{\bar{N}}_K^{e1}\cdot\bar{J} + (\Gamma + p)(\bar{I}_K\cdot\bar{d}_K^{e1}) \ , \tag{20}$$

with:

$$(N_K^{e1})_{gg'} = \frac{-e\mu_0\mu_N}{2\pi} \gamma_K g_K \sum_{g"} A_{g'g"} \sum_i \langle 0|r_{iK}^{-3}[(\bar{r}_{iK}\cdot\bar{r}_K)\delta(g,g") -$$

$$- (\bar{r}_K)_g\ (\bar{r}_{iK})_{g"}]|0\rangle \ , \tag{20a}$$

$$\bar{d}_K^{(e1)} = \frac{-e\mu_0\mu_N}{2\pi} \gamma_K g_K \sum_i F\langle 0|\bar{r}_{iK} \times \{(\bar{\rho} \times \bar{r}_K) - (\bar{\lambda} \times \bar{\sigma}_K)\}|0\rangle \ . \tag{20b}$$

(b) Second order.

The second order contribution is a sum of the terms:

$$\sum_n{}' \langle 0|h_2|n\rangle\langle n|h_2|0\rangle\ (E_0 - E_n)^{-1} = U + V + W \ , \tag{21}$$

where:

$$U = \sum_n{}' \langle 0|H_1|n\rangle\langle n|H_1|0\rangle\ (E_0 - E_n)^{-1} \ , \tag{21a}$$

$$V = \sum_n{}' \langle 0|H_1|n\rangle\langle n|H_{SR}^{(e)}|0\rangle\ (E_0 - E_n)^{-1} + c.c. \ , \tag{21b}$$

$$W = \sum_n{}' \langle 0|H_{SR}^{(e)}|n\rangle\langle n|H_{SR}^{(e)}|0\rangle\ (E_0 - E_n)^{-1} \ . \tag{21c}$$

We neglect the contribution of $\sum_i \gamma_K r_{iK}^{-3} (\bar{r}_{iK} \times \bar{v}_K)\cdot\bar{I}_K$ to $H_{SR}^{(e)}$ because this term is already taken into account in first order. Then $H_{SR}^{(e)}$ simplifies to:

$$H_{SR}^{(e)} = \frac{e\mu_0\mu_N}{4\pi m} \sum_i \sum_K g_K r_{iK}^{-3} (\bar{r}_{iK} \times \bar{p}_i)\cdot\bar{I}_K$$

$$= \frac{e\mu_0\mu_N}{4\pi m} \sum_K g_K \left(\frac{\bar{L}'}{r^3} \cdot \bar{I}_K \right) \quad , \tag{22}$$

with:

$$\left(\frac{\bar{L}'}{r^3}\right) = \sum_i (\bar{r}_{iK} \times \bar{p}_i)\, r_{iK}^{-3} \quad ,$$

where:

$\bar{p}_i = m\,\bar{v}_i$, and m is the electron mass.

By substituting H_1 of Eq.(11b) into Eq.(21a) we obtain for U :

$$U = \sum_n{}' \langle 0| -2\bar{L}\cdot\bar{\bar{A}}\cdot\bar{J} + \xi(\Gamma + p)|n\rangle\langle n| -2\bar{L}\cdot\bar{\bar{A}}\cdot\bar{J} + \xi(\Gamma + p)|0\rangle (E_0 - E_n)^{-1}$$

$$= \bar{J}\cdot\bar{\bar{A}}^{(e)}\cdot\bar{J} + (\bar{J}\cdot\bar{D}^{(e)})(\Gamma + p) + F^{(e)}(\Gamma + p)^2 \quad , \tag{23}$$

with:

$$A_{gg'}^{(e)} = 4 \sum_{g''} \sum_{g'''} A_{gg''} A_{g'g'''} \sum_n{}' \langle 0|L_{g''}|n\rangle\langle n|L_{g'''}|0\rangle (E_0 - E_n)^{-1} \quad ,$$

$$D_g^{(e)} = -2 \sum_{g'} A_{gg'} \sum_n{}' \langle 0|L_{g'}|n\rangle\langle n|\xi|0\rangle (E_0 - E_n)^{-1} + \text{c.c.} \quad ,$$

$$F^{(e)} = \sum_K \langle 0|\xi|n\rangle\langle n|\xi|0\rangle (E_0 - E_n)^{-1} \quad .$$

It is readily seen from these expressions that U can be absorbed in H_0 of Eq.(11a) as can be shown by a rather lengthy elementary calculation. The resulting new H_0 has the same form as Eq.(11a) with only slightly different values of F and the components of $\bar{\bar{A}}$ and $\bar{\rho}$ (or $\bar{\lambda}$). We neglect the term U in the following.

The next second-order contribution is:

$$V = \sum_n {}'\langle 0|H_1|n\rangle\langle n|H_{SR}^{(e)}|0\rangle\ (E_0 - E_n)^{-1} + c.c.$$

$$= \frac{e\mu_0\mu_N}{4\pi m} \sum_K \sum_n {}'\langle 0|\ -2\bar{L}\cdot\bar{\bar{A}}\cdot\bar{J} + \xi(\Gamma + p)|n\rangle\langle n|g_K(\frac{\bar{L}'}{r^3}\cdot\bar{I}_K)|0\rangle + c.c.$$

$$= \sum_K \bar{I}_K\cdot\bar{\bar{N}}_K^{e2}\cdot\bar{J} + (\Gamma + p)(\bar{I}_K\cdot\bar{d}_K^{e2})\ , \qquad (24)$$

with:

$$(N_K^{e2})_{gg'} = \frac{-e\mu_0\mu_N}{2\pi m} g_K \sum_{g''} A_{g'g''} \sum_n {}'\langle 0|L_{g''}|n\rangle\langle n|\frac{L'_g}{r^3}|0\rangle(E_0 - E_n)^{-1} + c.c.\ , \qquad (24a)$$

$$(\bar{d}_K^{e2})_g = \frac{+e\mu_0\mu_N}{4\pi m} g_K \sum_n {}'\langle 0|\xi|n\rangle\langle n|\frac{L'_g}{r^3}|0\rangle(E_0 - E_n)^{-1} + c.c. \qquad (24b)$$

The last second-order contribution is:

$$W = \sum_n {}'\langle 0|H_{SR}^{(e)}|n\rangle\langle n|H_{SR}^{(e)}|0\rangle\ (E_0 - E_n)^{-1}$$

$$= \left[\frac{e\mu_0\mu_N}{4\pi m}\right]^2 \sum_n {}'\langle 0|\sum_K g_K(\frac{\bar{L}'}{r^3}\cdot\bar{I}_K)|n\rangle\langle n|\sum_L g_L(\frac{\bar{L}'}{r^3}\cdot\bar{I}_L)|0\rangle$$

$$= \sum_{K,L} \bar{I}_K\cdot\bar{\bar{D}}_{KL}^{e}\cdot\bar{I}_L\ , \qquad (25)$$

with:

$$(D_{KL}^{e})_{gg'} = \left[\frac{e\mu_0\mu_N}{4\pi m}\right]^2 g_K g_L \sum_n {}'\langle 0|\frac{L'_g}{r^3}|n\rangle\langle n|\frac{L'_{g'}}{r^3}|0\rangle(E_0 - E_n)^{-1} + c.c. \qquad (25a)$$

This term is the so called indirect or electron-coupled spin-spin interaction. It can be neglected in most cases.

By combining Eqs.(17), (20), (24), and (25) we obtain:

$$H_{HF} = \sum_K \{\bar{I}_K\cdot\bar{\bar{N}}_K\cdot\bar{J} + (\Gamma + p)(\bar{I}_K\cdot\bar{d}_K) + \sum_{L>K} \bar{I}_K\cdot\bar{\bar{D}}_{KL}\cdot\bar{I}_L\}\ , \qquad (26)$$

where:

$$\bar{\bar{N}}_K = \bar{\bar{N}}_K^{n} + \bar{\bar{N}}_K^{e1} + \bar{\bar{N}}_K^{e2}\ , \qquad (26a)$$

$$\bar{d}_K = \bar{d}_K^n + \bar{d}_K^{e1} + \bar{d}_K^{e2} \quad . \tag{26b}$$

The first term of H_{HF} is the normal spin-rotation interaction, which is the same as in rigid rotor molecules. The second term is the spin-internal rotation interaction, which vanishes if $p \to 0$ and $\bar{\lambda} \to 0$. The last term is the spin-spin interaction.

The hyperfine Hamiltonian can be written in a different form, which is more convenient for calculating the matrix elements:

$$H_{HF} = \sum_K \{\bar{I}_K \cdot \bar{\bar{M}}_K \cdot \bar{J} + p(\bar{I}_K \cdot \bar{d}_K) + \sum_{L>K} \bar{I}_K \cdot \bar{\bar{D}}_{KL} \cdot \bar{I}_L\} \quad , \tag{27}$$

with:

$$(M_K)_{gg'} = (N_K)_{gg'} + \rho_g (d_K)_{g'} \quad .$$

The Hermitian form of this Hamiltonian is:

$$H_{HF} = \sum_K \{\tfrac{1}{2}(\bar{I}_K \cdot \bar{\bar{M}}_K \cdot \bar{J}) + \tfrac{1}{2}(\bar{I}_K \cdot \bar{\bar{M}}_K \cdot \bar{J})^\dagger + \tfrac{1}{2}(\bar{I}_K \cdot p\bar{d}_K) + \tfrac{1}{2}(\bar{I}_K \cdot p\bar{d}_K)^\dagger + \sum_{L>K} \bar{I}_K \cdot \bar{\bar{D}}_{KL} \cdot \bar{I}_L\} \quad . \tag{27a}$$

II. METHANOL-LIKE MOLECULES.

The preceeding treatment is subject to only one fundamental restriction, that the molecule has only one internal degree of freedom (α). Now we treat the more specific case of a molecule consisting of two parts , one part called the "top", is a symmetrical top and the other part, called the "frame", has a plane of symmetry, which contains the symmetry axis of the top. The top can rotate with respect to the frame about the symmetry axis with angular velocity $\dot{\alpha}$ (CH_3OH for example). We choose a right-handed coor-

dinate system fixed in the frame with the origin in the center of mass of the whole molecule. The z-axis of this system is parallel to the symmetry axis of the top, the x-axis is perpendicular to the plane of symmetry of the frame and the y-axis, lying in this plane, is perpendicular to both (Fig. 1, Appendix).

If A, B and C are the moments of inertia about the x, y and z-axis, respectively, -D the product of inertia I_{yz} ($I_{xy} = I_{xz} = 0$), C_2 the moment of inertia of the top about its symmetry axis, and $C_1 = C - C_2 = A - B$ we can write (see also (5, 6)) for H_0 (Eq.(18)):

$$H_0 = \frac{1}{2A} J_x^2 + \frac{1}{2(BC_1 - D^2)} \{C_1 J_y^2 + B J_z^2 + D(J_y J_z + J_z J_y) + \\ + 2D(pJ_y) + 2B(pJ_z) + \frac{BC - D^2}{C_2} p^2\} + V(\alpha) \qquad (28)$$

Explicit expressions for the components of $\bar{J}$ in the present frame of reference are given in the Appendix.

In the following we restrict ourselves to molecules with a threefold potential barrier $V(\alpha)$ and in particular to molecules whose top is formed by the methyl radical CH_3 . There are two problems that can be solved with great advantage using group-theoretical methods: (1) calculation of the eigenfunctions and eigenvalues of H_0 with an appropriate set of basis functions, and (2) determination of the wavefunctions, including the nuclear spin wavefunctions, which do not violate the Pauli-Exclusion Principle.

The molecular symmetry group.

It is readily shown that the Hamiltonian H_0 given in Eq.(28) is invariant under the following basic operations (and their pro-

ducts) of the internal symmetry group (7) : E (identity), C_3 and C_{2x}. Under these operations the components of $\bar{J}$, p and α transform as:

$$E : J_{x,y,z} \to J_{x,y,z} ; p \to p , \alpha \to \alpha$$

$$C_3 : J_{x,y,z} \to J_{x,y,z} ; p \to p , \alpha \to \alpha + \frac{2\pi}{3} \qquad (29)$$

$$C_{2x} : J_x \to J_x ; J_{y,z} \to -J_{y,z} ; p \to -p , \alpha \to -\alpha$$

These operations can be expressed in terms of the Euler angles ψ, θ and ϕ_1 , and the relative angle α:

$$E : \psi \to \psi ; \theta \to \theta ; \phi_1 \to \phi_1 ; \alpha \to \alpha$$

$$C_3 : \psi \to \psi ; \theta \to \theta ; \phi_1 \to \phi_1 ; \alpha \to \alpha + \frac{2\pi}{3} \qquad (30)$$

$$C_{2x} ; \psi \to \psi + \pi ; \theta \to \pi - \theta ; \phi_1 \to 2\pi - \phi_1 ; \alpha \to -\alpha$$

They constitute a group, which is isomorphic with the group C_{3v} with irreducible representations: A_1, A_2 and E.

The eigenfunctions of H_0 have the symmetry of the species A_1, A_2 or E. A method to obtain these eigenfunctions is given in the Appendix. The electric dipole moment of this type of molecules has the symmetry properties of A_2 , because it lies in the symmetry plane of the frame. The selection rules for the electric dipole transitions are easily derived from the Wigner-Eckart theorem as:

$$A_1 \leftrightarrow A_2 \quad \text{and} \quad E \leftrightarrow E .$$

Longuet-Higgins (8) determines the symmetry operations of the molecular group in a different way, which is more suitable for the nuclear spin wavefunctions. Let P be any permutation of the positi-

ons and spins of identical nuclei, or any product of such permutations. If E is the identity operation and E^* the operator inverting the positions of all particles in the center of mass, then the molecular symmetry group is a set of:

i) all feasible P, including E,

ii) all feasible products $P\,E^* = E^*\,P$,

where "feasible" means leaving the Hamiltonian invariant. The operation E^* ($J_x \rightarrow -J_x$, $J_y \rightarrow -J_y$, $J_z \rightarrow -J_z$; $\alpha \rightarrow \alpha$) and pèrmutations which merely exchange two protons in the CH_3-group ($J_x \rightarrow J_x$, $J_y \rightarrow J_y$, $J_z \rightarrow J_z$; $\alpha \rightarrow -\alpha$) do not satisfy the criterion of feasibility. The remaining operations, which do satisfy the requirements (i) and (ii) are:

1) identity E

2) cyclic permutations of the three protons in the methyl radical (C_3 and C_3^2)

3) permutations of only two protons followed by the inversion E^* (C_{2x} , $C_{2x}C_3$, $C_{2x}C_3^2$).

In the case of three equivalent protons, there are six independent spin wavefunctions, linear combinations of triple products of α_i and β_i , where α_i , β_i stands for the spin wavefunction of the i-th proton with spin up or down, respectively. This set generates a reducible representation of the group. The problem of finding the basis sets for the irreducible representations of the group C_{3v} reduces to the problem of finding them for the group S_3 , since all spin wavefunctions are invariant under the inversion E^*. This problem has been solved by Gunther-Mohr et.al. (1) and the result is reproduced in Table I. The spin wavefunctions are given in the

$|(I_1 I_2) I_{12}\ I_3\ I\ M_I\rangle$ representation, which corresponds to the coupling scheme:

$$\bar{I}_1 + \bar{I}_2 = \bar{I}_{12} \quad ,$$

$$\bar{I}_{12} + \bar{I}_3 = \bar{I} \quad ,$$

where $\bar{I}_1$, $\bar{I}_2$ and $\bar{I}_3$ are the spins of the three protons of the CH_3-group. The nuclear spins in the frame are taken into account later-on.

Table I. The spin basis functions of the irreducible representations of the group C_{3v} .

Basis functions $\|(I_1 I_2) I_{12}\ I_3\ I\ M_I\rangle$	Representation
$I_{12} = 1,\ I = 3/2,\ M_I = \pm 1/2, \pm 3/2$	A_1
$I_{12} = 1,\ I = 1/2,\ M_I = 1/2$ $I_{12} = 0,\ I = 1/2,\ M_I = 1/2$	E
$I_{12} = 1,\ I = 1/2,\ M_I = -1/2$ $I_{12} = 0,\ I = 1/2,\ M_I = -1/2$	E

In order to calculate the hyperfine structure of a certain rotational level, we have to determine a set of appropriate total wavefunctions, including nuclear spins, which satisfy the following conditions:

i) form a basis set for an irreducible representation of the molecular symmetry group,

ii) are not forbidden by the Pauli Exclusion Principle.

According to the last requirement, the total wavefunctions should be antisymmetric for exchange of two identical protons, and hence symmetric for a cyclic permutation of the three protons in the methyl radical (class $2C_3$). The exclusion principle is not committal for the operations PE^* belonging to the class $(3C_{2x})$, because they do not merely permute identical protons. We conclude that the total wavefunction should be of species A_1 or A_2 and that total wavefunctions of species E are forbidden.

The rotational levels are classified as species A_1 , A_2 or E. In the Appendix is shown that levels of species A can be denoted by $(J_{\gamma+})$ or $(J_{\gamma-})$ with eigenfunctions $|J_{\gamma+}\ M_J\rangle$ or $|J_{\gamma-}\ M_J\rangle$, respectively. The doubly degenerate levels of species E are denoted by $(J_{\gamma'})$ with eigenfunctions $|J_{\gamma'+}\ M_J\rangle$ and $|J_{\gamma'-}\ M_J\rangle$. The symbol $\gamma(\gamma')$ labels the rotational states with the same J. The transformation of the wavefunctions under the operation C_{2x} is given by: $C_{2x}\ |J_{\gamma\pm}\ M_J\rangle = \pm\ (-1)^J |J_{\gamma\pm}\ M_J\rangle$, both for functions of A and E species.

For the spin wavefunctions as given in Table I we use the shorthand notation $|I_{12}\ I\ M_I\rangle$ for $|(I_1 I_2) I_{12}\ I_3\ I\ M_I\rangle$. The set of functions, which are products of the rotational eigenfunctions $|J_{\gamma\pm}\ M_J\rangle$ and the spin wavefunctions $|I_{12}\ I\ M_I\rangle$ form a basis for a reducible representation of the symmetry group. This representation can be reduced by taking the proper linear combinations of these product functions. The result is given in Table II. Forbidden total

Table II. The total basis functions and their symmetry belonging to the rotational states.

ROTATIONAL				TOTAL		
State	Symmetry		Wavefunction	Basis functions [a]	Symmetry	
	J-even	J-odd			J-even	J-odd
$(J_{\gamma+})$	A_1	A_2	$\|J_{\gamma+}M_J\rangle$	$\|J_{\gamma+}M_J\rangle\|1\ \frac{1}{2}\ M_I\rangle$	A_1	A_2
$(J_{\gamma-})$	A_2	A_1	$\|J_{\gamma-}M_J\rangle$	$\|J_{\gamma-}M_J\rangle\|1\ \frac{1}{2}\ M_I\rangle$	A_2	A_1
(J_γ)	E	E	$\|J_{\gamma+}M_J\rangle$	$\frac{1}{\sqrt{2}}\{\|J_{\gamma-}M_J\rangle\|0\ \frac{1}{2}\ M_I\rangle + i\|J_{\gamma+}M_J\rangle\|1\ \frac{1}{2}\ M_I\rangle\}$	A_1	A_2
			$\|J_{\gamma-}M_J\rangle$	$\frac{1}{\sqrt{2}}\{\|J_{\gamma+}M_J\rangle\|0\ \frac{1}{2}\ M_I\rangle + i\|J_{\gamma-}M_J\rangle\|1\ \frac{1}{2}\ M_I\rangle\}$	A_2	A_1

[a] including the three proton spins in the top, but excluding other spins in the top or frame.

wavefunctions of species E are omitted.

The basis functions of Table II have to be extended with the spin wavefunctions $|I_N\ M_N\rangle$ of the nuclear spins $\bar{I}_N$ in the frame of the molecule. The basis functions in Table II, and hence also the extended total wavefunctions, are given in the uncoupled representation $|M_J\ ,\ M_I\ ,\ M_N\rangle$. In the absence of an external electric or magnetic field, however, it is more convenient to calculate the matrix elements of the Hamiltonian in the coupling scheme, in which the angular momenta $\bar{J}$, $\bar{I}$ and $\bar{I}_N$ are all coupled to the total angular momentum $\bar{F}$, since F and M_F are good quantum numbers in contrast to M_J , M_I and M_N . The wavefunctions corresponding to this coupling scheme (Eqs.(33) and (34)) are merely linear combinations of the uncoupled wavefunctions given in Table II and so have the same symmetry properties. From the Wigner-Eckart theorem it follows that all matrix elements between basis functions of different species vanish. The rotational part H_0 of the Hamiltonian is, of course, diagonal in all quantum numbers, but the hyperfine Hamiltonian H_{HF} is not. Since in general the hyperfine interactions are much weaker than molecular rotation, matrix elements of H_{HF} off-diagonal in the rotational quantum numbers J and $\gamma_{(\pm)}$ can be neglected. If the rotational splittings are very small (K-doublets) or zero (E-levels), these matrix elements vanish because of the symmetry. The Hamiltonian matrix splits into a number of submatrices that can be characterized by J and γ and symmetry type A_1 or A_2. The two submatrices of species A_1 and A_2, which belong to one particular rotational level (J_γ) of species E, are identical. This implies that the degeneracy is not lifted by the hyperfine interactions.

A. THE MATRIX ELEMENTS.

The most appropriate coordinate system for the calculation of the matrix elements of H_{HF} (Eq.(28)) is the space fixed CM-system (X,Y,Z). For this reason the Hamiltonian is transformed from the molecule fixed (x,y,z) to the space fixed (X,Y,Z) system. In order to calculate the matrix elements with tensor operator techniques (9) all operators of the hyperfine Hamiltonian are expressed in spherical tensor operators:

$$\bar{I}_K \cdot \bar{\bar{M}}_K \cdot \bar{J} = \sum_{\nu=0,1,2} (-)^{\nu} (2\nu+1)^{\frac{1}{2}} \{I_K^{(1)} \{M_K^{(\nu)} J^{(1)}\}^{(1)}\}^{(0)} ,$$

$$\left[\bar{I}_K \cdot \bar{\bar{M}}_K \cdot \bar{J}\right]^{\dagger} = \sum_{\nu=0,1,2} (2\nu+1)^{\frac{1}{2}} \{\{J^{(1)} M_K^{(\nu)}\}^{(1)} I_K^{(1)}\}^{(0)} ,$$

$$p(\bar{I}_K \cdot \bar{d}_K) = -\sqrt{3}\, \{I_K^{(1)} \{p^{(0)} d_K^{(1)}\}^{(1)}\}^{(0)} ,$$

$$\left[p(\bar{I}_K \cdot \bar{d}_K)\right]^{\dagger} = -\sqrt{3}\, \{\{d_K^{(1)} p^{(0)}\}^{(1)} I_K^{(1)}\}^{(0)} ,$$

$$\bar{I}_K \cdot \bar{\bar{D}}_{KL} \cdot \bar{I}_L = \sqrt{5}\, \{D_{KL}^{(2)} \{I_K^{(1)} I_L^{(1)}\}^{(2)}\}^{(0)} ,$$

$$= \sqrt{5}\, \{I_K^{(1)} \{D_{KL}^{(2)} I_L^{(1)}\}^{(1)}\}^{(0)} . \qquad (31)$$

with (10):

$$p_0^{(0)} = p \quad *) ,$$

$$V_{\pm 1}^{(1)} = \mp \left(\frac{1}{2}\right)^{\frac{1}{2}} (V_X \pm i V_Y) ,$$

$$V_0^{(1)} = V_Z ,$$

---

*) p is really a tensor of rank zero since it commutes with J_X, J_Y, and J_Z.

$$T^{(0)}_0 = -\left(\frac{1}{3}\right)^{\frac{1}{2}} (T_{XX} + T_{YY} + T_{ZZ}) \quad ,$$

$$T^{(1)}_{\pm 1} = \mp \frac{i}{2} \left[(T_{YZ} - T_{ZY}) \mp i(T_{ZX} - T_{XZ})\right] \quad ,$$

$$T^{(1)}_0 = \left(\frac{1}{2}\right)^{\frac{1}{2}} i(T_{XY} - T_{YX}) \quad ,$$

$$T^{(2)}_{\pm 2} = \frac{1}{2} \left[(T_{XX} - T_{YY}) \pm i(T_{XY} + T_{YX})\right] \quad ,$$

$$T^{(2)}_{\pm 1} = \frac{1}{2} \left[\mp(T_{XZ} + T_{ZX}) - i(T_{YZ} + T_{ZY})\right] \quad ,$$

$$T^{(2)}_0 = \left(\frac{1}{6}\right)^{\frac{1}{2}} (2T_{ZZ} - T_{XX} - T_{YY}) \quad , \qquad (32)$$

where $\bar{V}$ stands for $\bar{J}$, $\bar{I}_K$ or $\bar{d}_K$, and $\bar{\bar{T}}$ for $\bar{\bar{M}}_K$ or $\bar{\bar{D}}_{KL}$. The spherical tensor operators $D^{(0)}_{KL}$ and $D^{(1)}_{KL}$ are zero since $\bar{\bar{D}}_{KL}$ is a traceless and symmetric Cartesian tensor.

The hyperfine matrix elements for a molecule with three equivalent protons (spins $\bar{I}_1$, $\bar{I}_2$ and $\bar{I}_3$) in the top and one nuclear spin $\bar{I}_4$ located in the frame have been calculated, using the coupling scheme:

$$\bar{J} + \bar{I}_4 = \bar{F}_1 \ , \quad \bar{I}_1 + \bar{I}_2 = \bar{I}_{12} \ , \quad \bar{I}_{12} + \bar{I}_3 = \bar{I} \ , \quad \bar{F}_1 + \bar{I} = \bar{F} \ .$$

The corresponding set of basis functions for the rotational levels $(J_{\gamma\pm})$ of species A_1 or A_2 are:

$$\phi_\pm = \left|(J_{\gamma\pm} I_4) F_1, ((I_1 I_2) I_{12}{=}1, I_3) I{=}\frac{3}{2}, F, M_F\right> \quad , \qquad (33)$$

and for the rotational levels (J_γ) of species E:

$$\psi_\pm = \left(\frac{1}{2}\right)^{\frac{1}{2}} \left\{\left|(J_{\gamma\mp} I_4) F_1, ((I_1 I_2) I_{12}{=}0, I_3) I{=}\frac{1}{2}, F, M_F\right> + \right.$$

$$\left. + i\left|(J_{\gamma\pm} I_4) F_1, ((I_1 I_2) I_{12}{=}1, I_3) I{=}\frac{1}{2}, F, M_F\right>\right\} \quad . \qquad (34)$$

The basis functions $\phi_{\pm}$ and $\psi_{\pm}$ are constructed out of the (uncoupled) total basis functions of Table II and the spin wavefunctions $|I_4 M_4>$ of the frame using standard techniques. It should be noted that to a particular rotational level of species A belongs the set of functions ϕ_+ or ϕ_- but not both sets together, while to a particular rotational level of species E belong both sets of functions ψ_+ as well as ψ_-. The symmetry of the functions ϕ_+ or ϕ_- is that of the level to which they belong. The basis functions ψ_+ have symmetry A_1 or A_2 and ψ_- have symmetry A_2 or A_1 for J is even or odd, respectively, (Table II).

Defining $\phi'_{\pm}$ and $\psi'_{\pm}$ as the functions $\phi_{\pm}$ and $\psi_{\pm}$ with F_1, F, M_F replaced by F'_1, F', M'_F, respectively, we can write for the matrix elements:

$$<\phi_{\pm}| H_{HF} |\phi'_{\pm}> = A\, C^{(1)}_{J\gamma\pm} + B\, C^{(2)}_{J\gamma\pm} + P\, D^{(1)}_{J\gamma\pm} + Q\, D^{(2)}_{J\gamma\pm} \quad , \tag{35}$$

for the A-levels, and:

$$<\psi_+| H_{HF} |\psi'_+> = <\psi_-| H_{HF} |\psi'_-> = A\, C^{(1)}_{J\gamma} + B\, C^{(2)}_{J\gamma} + Q\, D^{(2)}_{J\gamma} \quad , \tag{36}$$

for the E-levels.

The matrix elements $<\psi_+| H_{HF} |\psi'_->$ are zero, because the wavefunctions ψ_+ and ψ_- have different symmetry. The terms in expression (36), which are mixed in I (I=0 and I=1) cancel; this can be proved using the hermiticity of the Hamiltonian.

The values of the coupling constants $C^{(i)}$ and $D^{(i)}$ depend on the rotational levels in question. They are labeled in the same way as the rotational levels ($J_{\gamma+}$ or $J_{\gamma-}$ for A-levels, and J_{γ} for

E-levels) to which they belong. The constant $C^{(1)}$ refers to the spin-rotation interaction of the three protons in the top; $C^{(2)}$ is the same for the nuclear spin $\bar{I}_4$ in the frame; $D^{(1)}$ is the coupling constant for the spin-spin interactions between the protons in the top, and $D^{(2)}$ is the coupling constant for the same interaction between the spin in the frame and the three proton spins in the top. The four coupling constants of an A-level are:

$$C^{(1)}_{J\gamma\pm} = \sum_{K=1}^{3} \left[CM_{K,J\gamma\pm} + Cd_{K,J\gamma\pm}\right] ,$$

$$C^{(2)}_{J\gamma\pm} = CM_{4,J\gamma\pm} + Cd_{4,J\gamma\pm} ,$$

$$D^{(1)}_{J\gamma\pm} = S_{12,J\gamma\pm} + S_{13,J\gamma\pm} + S_{23,J\gamma\pm} ,$$

$$D^{(2)}_{J\gamma\pm} = S_{14,J\gamma\pm} + S_{24,J\gamma\pm} + S_{34,J\gamma\pm} , \qquad (37)$$

and the three coupling constants for an E-level:

$$C^{(1)}_{J\gamma} = \tfrac{1}{2} \sum_{K=1}^{3} \left[(CM_{K,J\gamma+} + CM_{K,J\gamma-}) + (Cd_{K,J\gamma+} + Cd_{K,J\gamma-})\right] ,$$

$$C^{(2)}_{J\gamma} = \tfrac{1}{2} \left[(CM_{4,J\gamma+} + CM_{4,J\gamma-}) + (Cd_{4,J\gamma+} + Cd_{4,J\gamma-})\right] ,$$

$$D^{(2)}_{J\gamma} = \tfrac{1}{2} \sum_{K=1}^{3} \left[S_{K4,J\gamma+} + S_{K4,J\gamma-}\right] . \qquad (38)$$

The quantities CM_K , Cd_K and S_{KL} depend on the rotational wavefunction belonging to the rotational level in question. They carry as subscript the quantum numbers of this wavefunction. Explicit expressions for these quantities are:

$$CM_{K,J\gamma\pm} = \sum_{\nu=0,2} (2\nu+1)^{\frac{1}{2}} \begin{Bmatrix} 1 & 1 & \nu \\ J & J & J \end{Bmatrix} \langle J_{\gamma\pm} || M_K^{(\nu)} || J_{\gamma\pm} \rangle \ , \qquad (39)$$

$$Cd_{K,J\gamma\pm} = -\frac{1}{2}\left[J(J+1)(2J+1)\right]^{-\frac{1}{2}} \left[\langle J_{\gamma\pm} || \{p^{(0)} d_K^{(1)}\}^{(1)} || J_{\gamma\pm} \rangle + \right.$$

$$\left. + \langle J_{\gamma\pm} || \{d_K^{(1)} p^{(0)}\}^{(1)} || J_{\gamma\pm} \rangle \right] \ , \qquad (40)$$

$$S_{KL,J\gamma\pm} = \frac{2}{3} \left[\frac{3J(2J-1)}{(2J+1)(2J+2)(2J+3)} \right]^{\frac{1}{2}} \langle J_{\gamma\pm} || D_{KL}^{(2)} || J_{\gamma\pm} \rangle \ . \qquad (41)$$

The quantities A, B, P and Q used in Eqs.(35) and (36) are given by:

$$A = (-)^{J+2F_1'+F+I_4+I+1} \left[\sqrt{\frac{5}{3}} \delta(I,\tfrac{3}{2}) + \sqrt{\frac{1}{6}} \delta(I,\tfrac{1}{2}) \right] \left[(2F_1+1)(2F_1'+1) J(J+1)(2J+1) \right]^{\frac{1}{2}}$$

$$\times \begin{Bmatrix} F_1 & F_1' & 1 \\ J & J & I_4 \end{Bmatrix} \begin{Bmatrix} F_1 & F_1' & 1 \\ I & I & F \end{Bmatrix} \delta(F,F') \delta(M_F,M_F') \ ,$$

$$B = \frac{1}{2} \left[F_1(F_1+1) - I_4(I_4+1) - J(J+1) \right] \delta(F_1,F_1') \delta(F,F') \delta(M_F,M_F') \ ,$$

$$P = (-)^{J+2F_1'+F+I_4+I} \ \tfrac{1}{2}\sqrt{5} \left[\frac{(2F_1+1)(2F_1'+1)(2J+1)(2J+2)(2J+3)}{2J(J-1)} \right]^{\frac{1}{2}} \times$$

$$\times \begin{Bmatrix} F_1 & F_1' & 2 \\ J & J & I_4 \end{Bmatrix} \begin{Bmatrix} F_1 & F_1' & 2 \\ I & I & F \end{Bmatrix} \delta(F,F') \delta(M_F,M_F') \delta(I,\tfrac{3}{2}) \ ,$$

$$Q = (-)^{F_1'+I+F+1} \left[\frac{(2F_1+1)(2F_1'+1)(2J+1)(2J+2)(2J+3) I_4(I_4+1)(2I_4+1)}{2J(2J-1)} \right]^{\frac{1}{2}} \times$$

$$\times \left[\frac{5}{2}\sqrt{2} \delta(I,\tfrac{3}{2}) + \frac{1}{2}\sqrt{5} \delta(I,\tfrac{1}{2}) \right] \begin{Bmatrix} F_1 & F_1' & 1 \\ I & I & F \end{Bmatrix} \begin{Bmatrix} J & J & 2 \\ I_4 & I_4 & 1 \\ F_1 & F_1' & 1 \end{Bmatrix} \delta(F,F') \delta(M_F,M_F') \ , \qquad (42)$$

where I=3/2 for A-levels and I=1/2 for E-levels. The degeneracy of a hyperfine sublevel is (2F+1) and 2(2F+1) for a rotational level

of species A and E, respectively. The mutual spin-spin interactions between the protons in the top vanish for E-levels. In deriving Eqs.(36) and (38), use is made of the fact that the matrix elements should be invariant under a cyclic permutation of the protons in the top.

B. THE HYPERFINE COUPLING CONSTANTS.

All coupling constants can be written in terms of $\langle J_{\gamma\pm}||T^{(\nu)}||J_{\gamma\pm}\rangle$, where $T^{(\nu)}$ are spherical tensors of rank $\nu=0$, 1 or 2 (Eqs.(39-41)). These matrix elements can be evaluated with the aid of the Wigner-Eckart theorem:

$$\langle J_{\gamma\pm}||T^{(\nu)}||J_{\gamma\pm}\rangle = (-)^{J-M_J}\begin{pmatrix} J & \nu & J \\ -M_J & 0 & M_J \end{pmatrix}^{-1} \langle J_{\gamma\pm}M_J|T^{(\nu)}_0|J_{\gamma\pm}M_J\rangle$$

$$= \begin{pmatrix} J & \nu & J \\ -J & 0 & J \end{pmatrix}^{-1} \langle J_{\gamma\pm}J|T^{(\nu)}_0|J_{\gamma\pm}J\rangle. \quad (43)$$

The transformation of spherical tensor $T^{(\nu)}$ from the space-fixed to the molecular frame of reference, in which the tensor components are explicitly known, is given by:

$$T^{(\nu)}_{q'} = \sum_q (-)^q D^{(\nu)}_{q',q}(\psi,\theta,\phi_1)\ \tilde{T}^{(\nu)}_q \ ,$$

where $\tilde{T}^{(\nu)}_q$ are the tensor components in the molecular frame, and $D^{(\nu)}_{q',q}(\psi,\theta,\phi_1)$ are the elements of the representation matrix of 3-dimensional rotation. Hence:

$$\langle J_{\gamma\pm}||T^{(\nu)}||J_{\gamma\pm}\rangle = \begin{pmatrix} J & \nu & J \\ -J & 0 & J \end{pmatrix}^{-1} \sum_q (-)^q \langle J_{\gamma\pm}J|D^{(\nu)}_{0,q}\tilde{T}^{(\nu)}_q|J_{\gamma\pm}J\rangle. \quad (44)$$

This expression can be evaluated for molecules which are of nearly

symmetric-top type. In that case the rotational wavefunctions, which are series expansions (Appendix), can be approximated by (Eq. (A16), Appendix):

$$|J_{\gamma\pm}M_J\rangle = |JM_JK\tau\pm\rangle = \frac{1}{\sqrt{2}}(u^{JM}_{K\tau} \pm u^{JM}_{-K\tau'}) \quad , \tag{45}$$

with $K\geq 0$ and $(\tau,\tau') = (1,1)$, $(2,3)$ or $(3,2)$, depending on the value of K (M stands for M_J). The only exception is the A-type rotational level with K=0, which we shall exclude for the present, since the results are the same. The approximation Eq.(45) is extremely good for the rotational wavefunctions of CH_3OH with relatively low J-values (11). As pointed out in the Appendix, the subscript γ can be replaced by $K\tau$. The wavefunctions $u^{JM}_{K\tau}$ as given in Eq.(A6) can be rewritten in terms of the Euler angles ψ, θ and ϕ_1 of the molecule-fixed coordinate system defined in this section:

$$u^{JM}_{K\tau} = |JKM\rangle|\tau_K\rangle \quad , \tag{46}$$

where $|JKM\rangle$ are the symmetric top eigenfunctions and:

$$|\tau_K\rangle = \exp(-iK\alpha)\ P^{K\tau}(\alpha) \quad ,$$

where:

$$P^{K\tau}(\alpha) = \frac{1}{\sqrt{2\pi}} \sum_{l=-\infty}^{\infty} a^{K\tau n}_{(3l-\tau+1)}\ \exp\{i(3l-\tau+1)\alpha\} \quad ,$$

The coefficients $a^{K\tau n}_{s}$ are defined in the Appendix.

The difference in the expression of $|\tau_K\rangle$ above with the expression (A6) originates from the different choice of the molecular frame (x,y,z here and a,b,c in the Appendix). With the wavefunctions defined in Eqs.(45) and (46), Eq.(44) becomes now:

$$\langle JK\tau\pm||T^{(\nu)}||JK\tau\pm\rangle = \tfrac{1}{2}\begin{pmatrix} J & \nu & J \\ -J & 0 & J \end{pmatrix}^{-1} \times$$

$$\times \sum_q (-)^q \Big[\langle JKJ|D^{(\nu)}_{0,q}|JKJ\rangle\langle\tau_K|\tilde{T}^{(\nu)}_q|\tau_K\rangle + \langle J-KJ|D^{(\nu)}_{0,q}|J-KJ\rangle\langle\tau'_{-K}|\tilde{T}^{(\nu)}_q|\tau'_{-K}\rangle$$

$$\pm \langle JKJ|D^{(\nu)}_{0,q}|J-KJ\rangle\langle\tau_K|\tilde{T}^{(\nu)}_q|\tau'_{-K}\rangle \pm \langle J-KJ|D^{(\nu)}_{0,q}|JKJ\rangle\langle\tau'_{-K}|\tilde{T}^{(\nu)}_q|\tau_K\rangle\Big] \; . \tag{47}$$

By integrating over ψ, θ and ϕ_1 we get:

$$\langle JK\tau\pm||T^{(\nu)}||JK\tau\pm\rangle = (-)^{J+K}\,\tfrac{1}{2}\,(2J+1) \times$$

$$\times\Big[\begin{pmatrix} J & \nu & J \\ -K & 0 & K \end{pmatrix}\{\langle\tau_K|\tilde{T}^{(\nu)}_0|\tau_K\rangle + (-)^{\nu}\langle\tau'_{-K}|\tilde{T}^{(\nu)}_0|\tau'_{-K}\rangle\} \pm$$

$$\pm\begin{pmatrix} J & 2 & J \\ -K & 2 & -K \end{pmatrix}\{\langle\tau_K|\tilde{T}^{(2)}_2|\tau'_{-K}\rangle + \langle\tau'_{-K}|\tilde{T}^{(2)}_{-2}|\tau_K\rangle\}\delta(K,1)\delta(\nu,2)\Big] . \tag{48}$$

Substitution of this equation into Eqs.(39), (40) and (41), and evaluation of the 3-j symbols yields:

$$CM_{JK\tau\pm} = \frac{1}{2J(J+1)}\langle\tau_K|\{J(J+1) - K^2\}(M_{xx} + M_{yy}) + 2K^2 M_{zz}|\tau_K\rangle$$

$$\pm \tfrac{1}{2}\,\mathrm{Re}\,\langle\tau_K|M^{(2)}_2|\tau'_{-K}\rangle\delta(K,1) \; , \tag{49}$$

$$Cd_{JK\tau\pm} = \frac{-K}{J(J+1)}\,\mathrm{Re}\,\langle\tau_K|\,\frac{pd_z + d_z p}{2}\,|\tau_K\rangle \; , \tag{50}$$

$$S_{JK\tau\pm} = \frac{\sqrt{6}}{3(J+1)(2J+3)}\{3K^2 - J(J+1)\}\langle\tau_K|D^{(2)}_0|\tau_K\rangle \pm$$

$$\pm \frac{J}{2J+3}\,\mathrm{Re}\,\langle\tau_K|D^{(2)}_2|\tau'_{-K}\rangle \times \delta(K,1) \; . \tag{51}$$

For simplicity we have dropped from these formulae the characters, which label the nuclei. In deriving these equations, use has been made of the fact that: $|\tau'_{-K}\rangle^{\mathfrak{M}} = |\tau_K\rangle$; $(M^{(2)}_0)^{\mathfrak{M}} = M^{(2)}_0$; $(M^{(2)}_{-2})^{\mathfrak{M}} =$

$= M^{(2)}_{2}$; $(D^{(2)}_{0})^{*} = D^{(2)}_{0}$; $(D^{(2)}_{-2})^{*} = D^{(2)}_{2}$; $(d_z)^{*} = d_z$ and $p^{*} = -p$.

Substitution of Eqs.(49), (50), and (51) into Eqs.(37) and (38) gives the expressions for the hyperfine coupling constants. The terms off-diagonal in τ_K vanish only for the rotational levels of species E. It can be proved that each proton in the top has an equal contribution to the coupling constants. This is also evident because of the symmetry.

The tensor components $\{D_{KL}\}^{(2)}_{q}$ for K,L = 1,2,3 depend on the angle α as $\exp(-iq\alpha)$. So $\{D_{KL}\}^{(2)}_{0}$ is independent on α and its contribution to the spin-spin coupling constant $D^{(1)}_{J\gamma\pm}$ can be calculated from the geometry of the molecule. The contribution of $\{D_{KL}\}^{(2)}_{2}$, however, vanishes which can be shown by calculation. The value of the first spin-spin constant is then:

$$D^{(1)}_{JK\tau\pm} = \frac{3\mu_0\mu_N^2 g_H^2}{4\pi}\left[\frac{3K^2 - J(J+1)}{(J+1)(2J+3)}\right] r_{HH}^{-3} \quad , \tag{52}$$

where r_{HH} is the distance between two protons in the top.
The second spin-spin coupling constant $D^{(2)}_{J\gamma(\pm)}$ can be determined numerically by calculating the relevant integrals over α, if the geometry and the wavefunctions $|\tau_K>$ are known. This has been performed for some levels of the methanol molecule using a computer (11).

In the last Section we have excluded for simplicity the levels with K=0. The coupling constants for these levels, however, can be calculated in an analogous way as for other K-values. The results are also given by Eqs.(49), (50), (51), and (52) if we drop the ± signs labeling the coupling constants.

APPENDIX.

THE EIGENFUNCTIONS OF H_0.

The Hamiltonian H_0 is given in Eq.(28). The orientation of the molecule-fixed frame of reference (x,y,z) relative to the space-fixed frame (X,Y,Z) is described by the Euler angles ψ, θ, and ϕ_1. Using the convention of Edmonds (12) for the Euler angles we can write for the components of the angular momentum operators $\bar{J}$ and p in the (x,y,z) frame:

$$J_x = -i\hbar\{-\sin\phi_1 \cot\theta (\frac{\partial}{\partial\phi_1})_{\psi,\theta,\alpha} + \cos\phi_1 (\frac{\partial}{\partial\theta})_{\psi,\phi_1,\alpha} + \frac{\sin\phi_1}{\sin\theta}(\frac{\partial}{\partial\psi})_{\phi_1,\theta,\alpha}\}$$

$$J_y = -i\hbar\{-\cos\phi_1 \cot\theta (\frac{\partial}{\partial\phi_1})_{\psi,\theta,\alpha} - \sin\phi_1 (\frac{\partial}{\partial\theta})_{\psi,\phi_1,\alpha} + \frac{\cos\phi_1}{\sin\theta}(\frac{\partial}{\partial\psi})_{\phi_1,\theta,\alpha}\}$$

$$J_z = -i\hbar (\frac{\partial}{\partial\phi_1})_{\psi,\theta,\alpha} ,$$

$$p = -i\hbar (\frac{\partial}{\partial\alpha})_{\psi,\theta,\phi_1} . \qquad \text{(A1)}$$

These components satisfy the commutation relations:

$$[J_i,J_j] = -i\hbar J_k \quad (i,j,k = x,y,z \text{ in cyclic order})$$

$$[J_i,p] = 0 \qquad \text{(A2)}$$

In order to reduce the coupling between J_z and p by a factor $\frac{D^2}{BC}$ the Nielson transformation is applied:

$$\theta' = \theta, \quad \psi' = \psi, \quad \phi' = \phi_1 - \frac{C_2}{C}\alpha, \quad \alpha' = \alpha, \quad , \qquad \text{(A3)}$$

(α is related to the Euler angles ϕ_1 and ϕ_2 of the two groups of the molecule as: $\alpha=\phi_1-\phi_2$). This transformation is equivalent to a

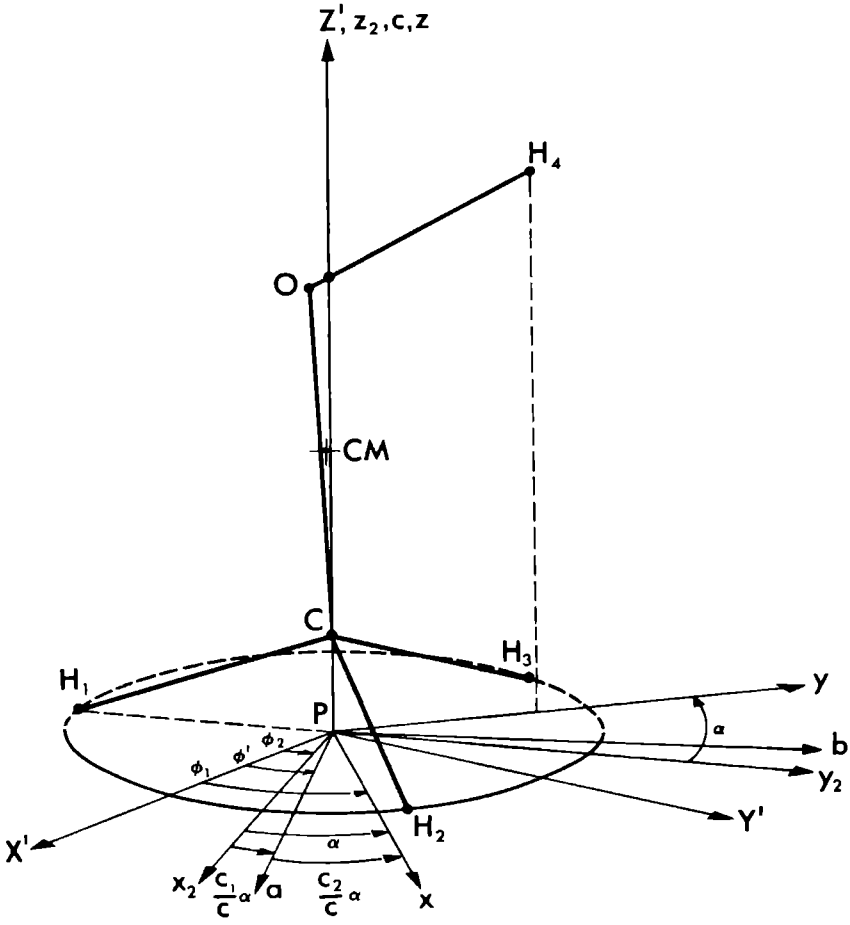

Fig.1. The methanol molecule with coordinate systems: (x,y,z) fixed to the "frame", (x_2,y_2,z_2) fixed to the "top", and (a,b,c) fixed to the molecule. The coordinate system (X',Y',Z') is the space fixed coordinate system (X,Y,Z) after a rotation over the Euler angle ψ about the Z-axis, followed by a rotation over the Euler angle θ about the new Y'-axis. All coordinate systems have their origin in the center of mass (CM). For clarity they are drawn after a translation of the origin to P.

rotation about the z-axis over an angle $\frac{C_2}{C}\alpha$, resulting in a coordinate system (a,b,c) with Euler angles ψ', θ', and ϕ' (Fig.1). This system is molecule-fixed, but not longer fixed to the frame (or to the top). The angular momentum operators J_a, J_b, J_c, and p' in the new frame are also given by Eq.(A1) if ψ, θ, ϕ_1 and α is replaced by ψ', θ', ϕ' and α', respectively, and the same commutation relations hold. Both sets of angular momenta are related by the following expressions:

$$
\begin{aligned}
J_x &= \cos(\tfrac{C_2}{C}\alpha)\, J_a + \sin(\tfrac{C_2}{C}\alpha)\, J_b \ , \\
J_y &= -\sin(\tfrac{C_2}{C}\alpha)\, J_a + \cos(\tfrac{C_2}{C}\alpha)\, J_b \ , \\
J_z &= J_c \ , \\
p &= p' - \frac{C_2}{C} J_c \ .
\end{aligned}
\tag{A4}
$$

By substituting Eqs.(A1)-(A4) into Eq.(28) the latter equation transforms into:

$$H_0 = H_I + H_{II} + H^+_{III} + H^-_{III} + H^+_{IV} + H^-_{IV} \ , \tag{A5}$$

with:

$$
\begin{aligned}
H_I &= \frac{(A+B)C_1 - D^2}{4A(BC_1 - D^2)} (J^2 - J_c^2) + \frac{1}{2C} J_c^2 + \frac{C}{2C_1C_2} p'^2 + V(\alpha) \ , \\
H_{II} &= \frac{D^2}{2C_1(BC_1 - D^2)} \left[\frac{C_1^2}{C^2} J_c^2 + \frac{2C_1}{C} p' J_c + p'^2 \right] \ , \\
H^{\pm}_{III} &= \frac{\mp iD}{2(BC_1 - D^2)} \exp(\pm i \tfrac{C_2}{C}\alpha)\, J_{\pm} \, (\pm \tfrac{1}{2}\hbar + p' + \frac{C_1}{C} J_c) \ , \\
H^{\pm}_{IV} &= \frac{(A-B)C_1 + D^2}{8A(BC_1 - D^2)} \exp(\pm 2i \tfrac{C_2}{C}\alpha)\, J_{\pm}^2 \ .
\end{aligned}
$$

with:

$$J_{\pm} = - (J_a \mp iJ_b)$$

The first term (H_I) of the Hamiltonian H_0 is a Hamiltonian of a symmetric top molecule with internal rotation. The terms H_{II}, $H^{\pm}_{III}$ and $H^{\pm}_{IV}$ are due to the asymmetry of the molecule. They can be considered as small pertubations on H_I, if the molecule is nearly a symmetric top as in the case of CH_3OH. The eigenfunctions of H_I have been calculated by Koehler and Dennison (13), and Verhoeven (14). Their result is:

$$u^{JM}_{K\tau n} = |JKM\rangle |\tau_{Kn}\rangle \ , \tag{A6}$$

where $|JKM\rangle$ are the normal symmetric top wavefunctions and:

$$|\tau_{Kn}\rangle = \exp(-iK\frac{C_1}{C}\alpha) \ p^{K\tau n}(\alpha) \ , \tag{A7}$$

with:

$$p^{K\tau n}(\alpha) = \frac{1}{\sqrt{2\pi}} \sum_{l=-\infty}^{\infty} a^{K\tau n}_{(3l-\tau+1)} \exp\{i(3l-\tau+1)\alpha\} \ ; \ \tau = 1,2,3,$$

are the solutions of the Mathieu differential equations. The coefficients $a^{K\tau n}_s$ in the Fourrier-expansion are tabulated for methanol in Refs. (15) and (16). In the following we shall restrict ourselves to n=0, and drop n from $u^{JM}_{K\tau n}$ and $|\tau_{Kn}\rangle$.

For the calculation of the matrix elements of H on this basis of $u^{JM}_{K\tau}$ we consider symmetry properties of these functions under the operations of the symmetry group of the Hamiltonian, in order to determine the structure of the energy matrix.

The group operations as described in Eq.(30) are in terms of the Euler angles (ψ', θ', ϕ') and α' given by:

$$E \quad : \psi' \to \psi' \quad ; \theta' \to \theta' \quad ; \phi' \to \phi' \quad ; \alpha' \to \alpha'$$

$$C_3 \quad : \psi' \to \psi' \quad ; \theta' \to \theta' \quad ; \phi' \to \phi' - \frac{2\pi}{3} \times \frac{C_1}{C} \quad ; \alpha' \to \alpha' + \frac{2\pi}{3}$$

$$C_{2x} : \psi' \to \psi' + \pi \quad ; \theta' \to \pi - \theta' \quad ; \phi' \to 2\pi - \phi' \quad ; \alpha' \to -\alpha' \qquad (A8)$$

A set of functions $u^{JM}_{K\tau}$ with the same J, M and absolute value of K (six if $K \neq 0$ and three if $K=0$) form a basis for a reducible representation of the group. This can be proved by using the relations $a^{K1}_{s} = a^{-K1}_{-s}$ and $a^{K2}_{s} = a^{-K3}_{-s}$ of the coefficients in the expansion of $|\tau_K\rangle$. The result of the decomposition of the representation into its constituent irreducible representations, together with the correct basis functions are given in Table III.

All functions Ψ as given in Table III transform under the C_3 group-operation as $C_3\Psi = \exp(\frac{2\pi}{3}\,\sigma\, i)\Psi$. The A_1 functions are symmetric under the C_{2x} operation and the A_2 functions are antisymmetric. A set of E type functions (Ψ_1 , Ψ_2) transforms under the C_{2x} operation as: $C_{2x}\Psi_1 = (-)^J\Psi_2$ and $C_{2x}\Psi_2 = (-)^J\Psi_1$. Since the Hamiltonian H_0 is clearly of species A_1, we can use the results obtained by the Wigner Eckart theorem (9). The matrix of the Hamiltonian reduces to four submatrices, the first one with basis functions of species A_1 ($\sigma=0$), the second one with basis functions of species A_2 ($\sigma=0$) and the last two, which are identical, with basis functions of species E ($\sigma=1$ and $\sigma= -1$, respectively).

The eigenfunctions of H_0 are*) :

---

*) These eigenfunctions are in perfect agreement with those of Verhoeven (14) but not with those given by Ivash et al (15). Although both authors calculate them in the same manner (not using group theory) the difference may be a question of phase convention.

Table III. The basis functions Ψ of the irreducible representations (column 1) of the group C_{3v}; n = 0,1, 2,.. ; σ (last column) determines the symmetry of Ψ under the group operation C_3 ($C_3\Psi = \exp(\frac{2\pi}{3}\sigma i)\Psi$).

REPRESENTATION	BASIS FUNCTIONS Ψ				σ
	K = 0	K = 3n (n≠0)	K = 3n + 1	K = 3n + 2	
A_1	u_{01}^{JM} [a]	$\frac{1}{\sqrt{2}}\{u_{K1}^{JM} + (-)^J u_{-K1}^{JM}\}$	$\frac{1}{\sqrt{2}}\{u_{K3}^{JM} + (-)^J u_{-K2}^{JM}\}$	$\frac{1}{\sqrt{2}}\{u_{K2}^{JM} + (-)^J u_{-K3}^{JM}\}$	0
A_2		$\frac{1}{\sqrt{2}}\{u_{K1}^{JM} - (-)^J u_{-K1}^{JM}\}$	$\frac{1}{\sqrt{2}}\{u_{K3}^{JM} - (-)^J u_{-K2}^{JM}\}$	$\frac{1}{\sqrt{2}}\{u_{K2}^{JM} - (-)^J u_{-K3}^{JM}\}$	0
E	u_{03}^{JM}	u_{K3}^{JM}	u_{K2}^{JM}	u_{K1}^{JM}	1
	u_{02}^{JM}	u_{-K2}^{JM}	u_{-K3}^{JM}	u_{-K1}^{JM}	-1
E		u_{-K3}^{JM}	u_{-K1}^{JM}	u_{-K2}^{JM}	1
		u_{K2}^{JM}	u_{K1}^{JM}	u_{K3}^{JM}	-1

[a] u_{01}^{JM} is of species A_1 or A_2 for J even or odd.

$$\left.\begin{array}{l}\text{(i) Species } A_1 \text{ (J even)} \\ \qquad\quad \text{or } A_2 \text{ (J odd)}\end{array}\right\} \; |J_{\gamma+}\, M_J> = a_0 u^{JM}_{01} + \sum_{K>0} \frac{a_K}{\sqrt{2}}(u^{JM}_{K\tau} + u^{JM}_{-K\tau'}) \tag{A9}$$

$$\left.\begin{array}{l}\text{(ii) Species } A_2 \text{ (J even)} \\ \qquad\quad \text{or } A_1 \text{ (J odd)}\end{array}\right\} \; |J_{\gamma-}\, M_J> = \sum_{K>0} \frac{b_K}{\sqrt{2}}(u^{JM}_{K\tau} - u^{JM}_{-K\tau'}) \;, \tag{A10}$$

where:

$\tau=1,\ \tau'=1$ if $K=3n$ with $n=1,2,3,\ldots$

$\tau=3,\ \tau'=2$ if $K=3n+1$ with $n=0,1,2,\ldots$

$\tau=2,\ \tau'=3$ if $K=3n+2$ with $n=0,1,2,\ldots$

These wavefunctions belong to the energy levels denoted by $(J_{\gamma+})$ or $(J_{\gamma-})$, where γ labels the A_1 or A_2-levels with the same J.

$$\text{(iii) Species E} \begin{cases} \Phi_1 = \sum_{K\tau} c_{K\tau}\, u^{JM}_{K\tau} \;, \\ \Phi_{-1} = \sum_{K\tau} d_{K\tau}\, u^{JM}_{K\tau} \;, \end{cases} \tag{A11}$$

where the sums run over all values of $K\tau$ with $\sigma=1$ or $\sigma=-1$ for Φ_1 or Φ_{-1}, respectively. The coefficients $c_{K\tau}$ and $d_{K'\tau'}$ are equal if the corresponding wavefunctions $u^{JM}_{K\tau}$ and $u^{JM}_{K'\tau'}$ form a basis for the E-representation (see Table III). Every linear combination of Φ_1 and Φ_{-1} is also an eigenfunction of the Hamiltonian and forms together with another independent linear combination of Φ_1 and Φ_{-1} a basis for the E-representation. In analogy with the A-levels, we choose for a particular E-level as eigenfunctions:

$|J_{\gamma\pm}> = \frac{1}{\sqrt{2}}(\Phi_1 \pm \Phi_{-1})$ or:

$$\text{E-level} \begin{cases} |J_{\gamma+}\, M_J> = \sum_K c_{K\tau} \frac{1}{\sqrt{2}}(u^{JM}_{K\tau} + u^{JM}_{-K\tau'}) \;, \\ |J_{\gamma-}\, M_J> = \sum_K c_{K\tau} \frac{1}{\sqrt{2}}(u^{JM}_{K\tau} - u^{JM}_{-K\tau'}) \;, \end{cases} \tag{A12}$$

with:

$$\left.\begin{array}{llllll} \tau=3 & \text{and} & \tau'=2 & \text{if} & K=3m \\ \tau=2 & \text{and} & \tau'=3 & \text{if} & K=3m+1 \\ \tau=1 & \text{and} & \tau'=1 & \text{if} & K=3m+2 \end{array}\right\} \quad m=0, \pm1, \pm2, \ldots$$

The corresponding levels are denoted by (J_γ), where γ labels the levels with the same J. Both choices (Eqs.(A11) and (A12)) of the E-levels are, of course, equivalent. The first one (Eq.(A11)) is the most common in litterature; all functions have a definite parity for the C_3 operation ($\exp(\frac{2\pi}{3}\sigma i)$). We prefer the latter one (Eq. (A12)), because the calculation of the hyperfine structure is easier in that case; both the A and E eigenfunctions have a definite parity for the C_{2x} operation:

$$C_{2x}\ |J_{\gamma\pm}\ M_J> = \pm\ (-)^J\ |J_{\gamma\pm}\ M_J> \ .$$

The coefficients $a_{K\tau}$, $b_{K\tau}$ and $c_{K\tau}$ of the eigenfunctions can be calculated by diagonalizing the Hamiltonian matrix. The matrix elements are easily derived from Eq.(A5). They are given in the following equations, using the shorthand notation: $H^{JK\tau}_{JK'\tau'} = \langle u^{JM}_{K\tau}|H_0|u^{JM}_{K'\tau'}\rangle$

$$H^{JK\tau}_{JK\tau} = (H_I)^{JK\tau}_{JK\tau} + (H_{II})^{JK\tau}_{JK\tau} = \hbar^2\,\frac{(A+B)C_1-D^2}{4A(BC_1-D^2)}\,(J^2+J-K) + \frac{\hbar^2}{2C}\,K^2 + E^{K\tau} +$$

$$+\ \hbar^2\,\frac{D^2}{2C_1(BC_1-D^2)}\left[\frac{C_1^2}{C^2}\,K^2 - \frac{C_1}{\pi C}\,iK\int_0^{2\pi}\{P^{K\tau}(\alpha)\}^*\,\frac{d}{d\alpha}P^{K\tau}(\alpha)\,d\alpha -\right.$$

$$\left. -\ \frac{1}{2\pi}\int_0^{2\pi}\{P^{K\tau}(\alpha)\}^*\,\frac{d^2}{d\alpha^2}\,P^{K\tau}(\alpha)\,d\alpha\right] , \qquad \text{(A13)}$$

$$H^{JK\tau}_{JK\pm1\tau'} = (H^{\mp}_{III})^{JK\tau}_{JK\pm1\tau'} = \hbar^2\,\frac{iD}{2(BC_1-D^2)}\,\{(J\mp K)(J\pm K+1)\}^{\frac{1}{2}}\ \times$$

$$\times \frac{1}{2\pi} \int_0^{2\pi} \left[\mp ie^{\mp i\alpha} \{P^{K\tau}(\alpha)\}^* \frac{d}{d\alpha} P^{K\pm 1\tau'}(\alpha) - \tfrac{1}{2} e^{\mp i\alpha} \{P^{K\tau}(\alpha)\}^* P^{K\pm 1\tau'}(\alpha) \right] d\alpha \tag{A14}$$

$$H^{JK\tau}_{JK\pm 2\tau'} = (H^{\mp}_{IV})^{JK\tau}_{JK\pm 2\tau'} = \hbar^2 \frac{(A-B)C_1 + D^2}{8A(BC_1 - D^2)} \{(J\mp K)(J\mp K-1)(J\pm K+1)(J\pm K+2)\}^{\frac{1}{2}}$$

$$\times \frac{1}{2\pi} \int_0^{2\pi} \{P^{K\tau}(\alpha)\}^* e^{\mp 2i\alpha} P^{K\pm 2\tau'}(\alpha) \, d\alpha \tag{A15}$$

All other matrix elements are zero. The differences between the equations above and those of Ref. (17) are merely introduced by a different choice of the Euler angles.

For slightly asymmetric top molecules the off-diagonal matrix elements are small. This implies that one term in the expansion of the eigenfunctions (Eqs. (A9), (A10), (A11), and (A12)) will be dominant. This gives a possibility to specify in a unique way the label γ of the energy levels and wavefunctions as: $\gamma = K\tau$ with $K>0$ if $(u^{JM}_{K\tau} \pm u^{JM}_{-K\tau'})$ is the dominant term. So levels of species A are denoted by $(JK\tau\pm)$ with eigenfunctions $|JM_J K\tau\pm\rangle$ and the levels of species E are denoted by $(JK\tau)$ with eigenfunctions $|JM_J K\tau+\rangle$ and $|JM_J K\tau-\rangle$.

Molecules such as methanol are in very good approximation symmetric top molecules. In this case the wavefunctions both of A and E-type levels can be approximated by the dominant term only (11):

$$|JM_J K\tau\pm\rangle = \frac{1}{\sqrt{2}} (u^{JM}_{K\tau} \pm u^{JM}_{-K\tau'}) \quad , \tag{A16}$$

with $K\geq 0$ and $(\tau,\tau') = (1,1)$, $(2,3)$ or $(3,2)$ depending on the value of K, except for the A-type levels with $K=0$, whose eigenfunctions are approximated by:

$$|JM_J01\rangle = u_{01}^{JM} \quad . \tag{A17}$$

These approximations are extremely good for the purpose of calculating the hyperfine coupling constants (of course not for the calculation of the rotational energies).

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CHAPTER 3

MEASUREMENTS AND RESULTS ON CH_3OH

I. INTRODUCTION.

We have performed accurate measurements on the hyperfine structure of the following transitions of methanol (CH_3OH): $(JK\tau) = (0,0,1) \rightarrow (1,0,1)$ at about 48 GHz; $(J,1,3-) \rightarrow (J,1,3+)$ for J = 2, 3 and 6 at about 2.5, 5, and 17 GHz, respectively. The last three transitions will be called the J = 2, 3 and 6 transitions in the following.

Except for the J = 0 level all other energy levels of methanol involved in the transitions are split because of the hyperfine interactions discussed in Chap. 2. The number of sublevels is six for J = 1 and eight for all J > 1. Hence, the spectrum of the $J = 0 \rightarrow 1$ transition consists of six hyperfine components, while the spectrum of the J = 2, 3 and 6 will contain a large number of them. Explicit calculation of the relative intensities shows that eight of these components will be by far dominant.

The hyperfine interactions are the nuclear spin-spin and spin-rotation interactions, as described in the previous Chapter. The strength of the spin-spin interactions can be calculated and is of the order of 10 kHz. The strength of the spin-rotation interactions cannot be calculated in advance, but is estimated to be of the same order of magnitude as in the rigid rotor molecules. The quadrupole hyperfine interactions are absent in normal methanol because $^{12}CH_3OH$ contains only nuclei with spin 0 or $\frac{1}{2}$. Hence, the

hyperfine splitting of the rotational transitions was expected to be of the order of 10 kHz.

II. SPECTROMETERS AND EXPERIMENTAL METHOD.

The J = 2, 3 and 6 transitions were investigated with the beam-maser spectrometer (BMS Fig.1) described by Bluyssen (1). The source of the molecular beam was a crinckly foil effuser, 1 cm in diameter, containing about 4 000 channels. The source pressure was a few Torr's resulting in a flux of 10^{19} mol/sec. The state selector was an electrostatic octupole, constructed of highly polished cylindrical stainless steel rods, 28 cm long. The positively and negatively charged rods are separately mounted on sheaves of perspex

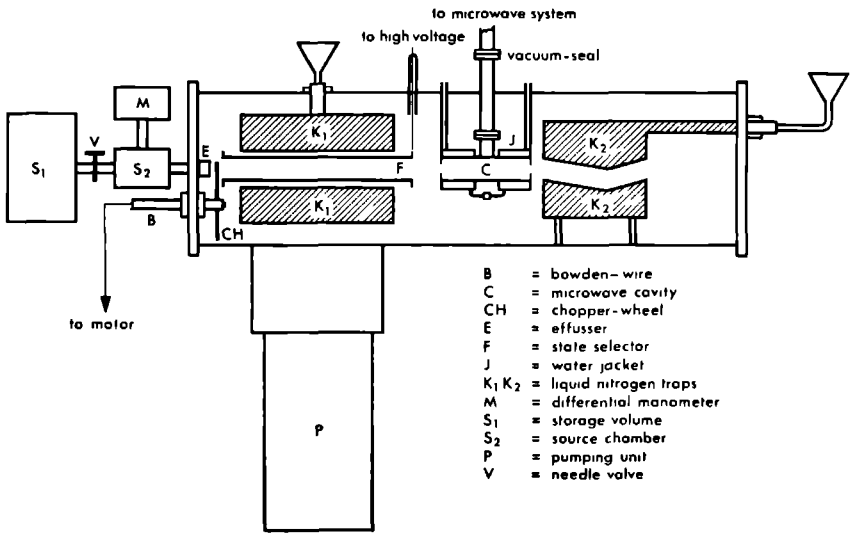

Fig.1. Schematic diagram of the beam-maser spectrometer (from: H. Bluyssen (1)).

providing good electrical isolation. The applied voltage was ± 35 kV yielding a maximum field of about 140 kV/cm between the neighbouring rods. The state selector was mounted inside a liquid nitrogen trap which trapped molecules deflected out of the beam. The experiments have been performed with cylindrical cavities, oscillating in the TM_{010} mode. The length of the cavities was 28, 100, and 30 cm for the J = 2, 3, and 6 transitions, respectively. The corresponding theoretical half-width due to the Heisenberg broadening is about 1.0, 0.3, and 0.9 kHz. The half-width could not be verified experimentally because none of the spectra contains a single line. The power emitted by the molecular beam (10^{-10} - 10^{-12} W) was detected by a superheterodyne system with phase sensitive demodulation. Modulation is achieved by mechanical chopping of the beam at 120 Hz. The detection scheme is shown in Fig. 2. Separate signal (SO) and local oscillator (LO) klystrons are employed with an intermediate frequency of 30 MHz. An automatic frequency control system using Schomandl FDS30 syncriminator phase-locks the LO-klystron at 30 MHz off the SO-frequency. The SO-klystron is coupled in the same way to a combined Schomandl-Rohde & Schwarz frequency system. The latter system consists of the Schomandl ND30M variable oscillator (300 Hz - 31 MHz) and the Rohde & Schwarz XUC frequency synthesizer (470-1000 MHz) both driven by a 10 MHz signal from the Rohde & Schwarz XSU oscillator. This oscillator is coupled to a Varian R20 rubidium frequency standard (5 MHz). At the crystal M higher harmonics of the frequency of the synthesizer are generated and mixed with the SO-frequency. The resulting 30 MHz beat frequency is used for the stabilization of the SO-klystron by a FDS30

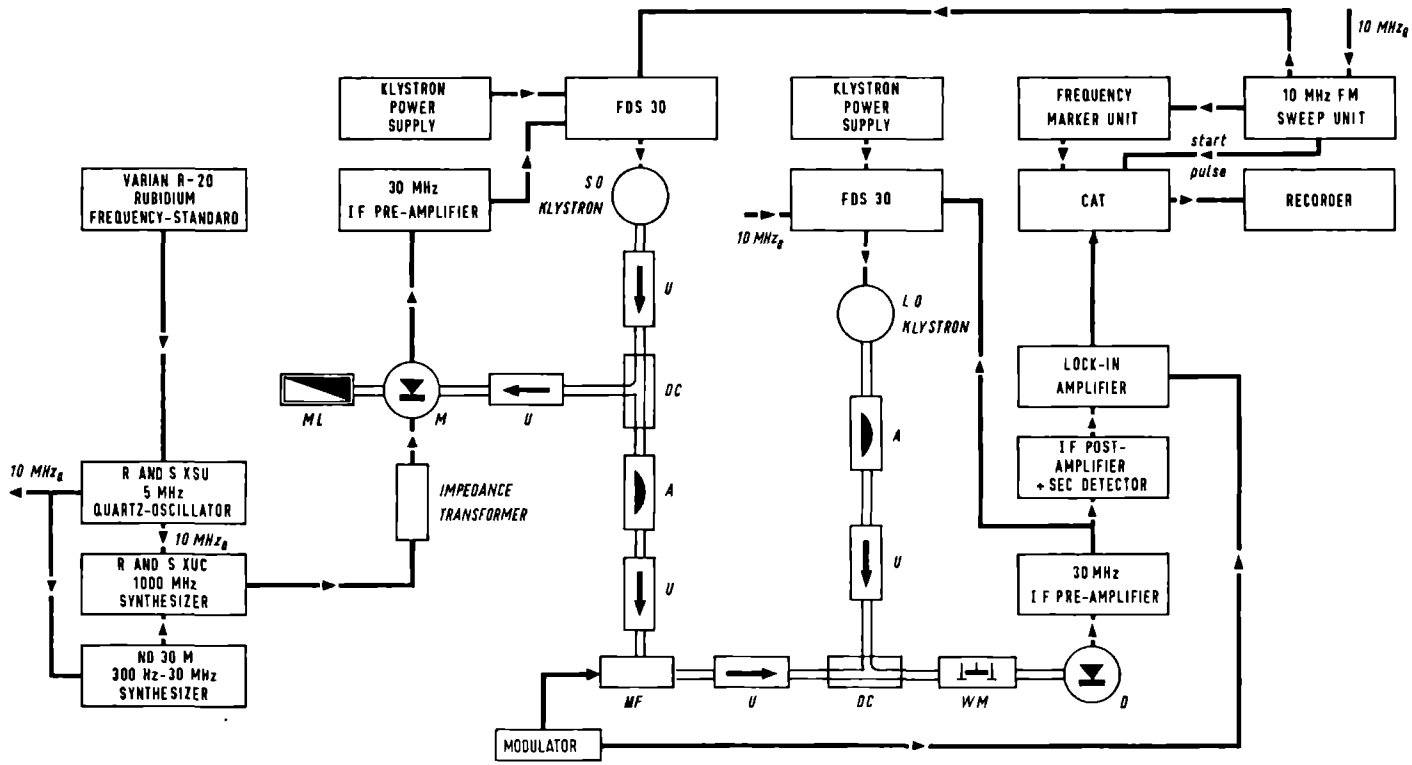

Fig.2. Superheterodyne detection scheme; A = attenuator; DC = directional coupler; U = ferrite isolator; ML = matched load; D = mixer crystal; M = multiplier crystal; WM = wave meter; MF = microwave field: cavity in the BMS or parallel plate cell in the BAS; Modulator = beam chopper in the BMS or square wave Stark generator in the BAS.

syncriminator.

For all investigated transitions the signal to noise ratio at the output of the lock-in amplifier was insufficient for good results. In order to increase the signal to noise ratio, time averaging techniques were employed with a computer of average transients (CAT, *Technical Measurements Corporation*). Exactly the same frequency region of the spectrum (typically 50 - 100 kHz) was scanned in a period of 20 seconds and added in the memory of the CAT (400 channels). The scanning was accomplished by sweeping the 10 MHz reference signal of the FDS30 syncriminator of the SO-klystron with a signal generated in a 10 MHz sweep unit. A typical number of scans was 100 - 200. The RC-time of the lock-in amplifier was set at 0.3 or 1 second, depending on the frequency region. With the CAT the signal to noise ratio increases as the square root of the number of scans. A detailed description of the detection system is found in Ref.(2).

The reflex klystrons used for the transitions at 2.5, 5 and 17 GHz were Sanders no 6455, Varian X26E and Varian X12 , respectively. The signal to noise ratio of the measured spectra of the J = 3 and 6 transitions was about 50, of the J = 2 transition about 25. The latter transition was investigated with a coaxial microwave system, the other ones with waveguide systems.

The J = 0 → 1 transition at 48 GHz was investigated with the beam-absorbtion spectrometer (BAS) developed by Huiszoon (3, 4). As a detailed description of the spectrometer can be found in the references mentioned above, only a general outline is given below (Fig.3). The absorption cell consists of two electrically isolated

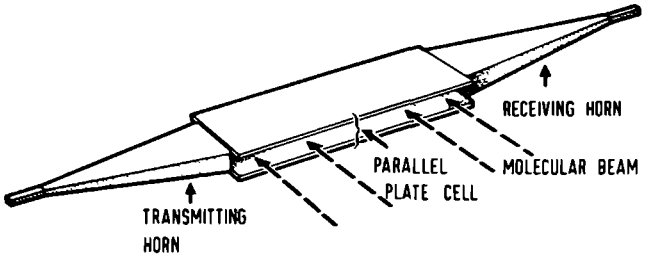

Fig.3. The absorption cell with horns. The direction of the molecular beam is indicated by arrows (from: C.Huiszoon (3)).

flat copper plates, 40 cm long, 10 cm wide, separated by a distance of 1 cm. The microwave radiation is sent between the plates by a transmitting horn and received by an identical horn. The aperture of the horns is 10 × 90 mm and the length is 300 mm. The horns are made of copper plates, simply screwed together. Between the horns and the cell, two cylindrical lenses are mounted, providing flat wavefronts of the microwave field propagating through the cell. The lenses are made of Rexolite 1422 (American Enkalon Division, USA). The propagation mode is essentially TEM with the E-vector perpendicular to the plates. The source of the molecular beam is a crinckly foil effuser 350 mm long and 4 mm wide, containing about 16 000 channels. Between the effuser and the parallel plate cell a diaphragm at liquid nitrogen temperature serves to trap molecules not travelling in the direction perpendicular to the direction of the propagation of the microwave radiation. In the diaphragm are mounted parallel copper screens, 50 mm long, at a distance of 2 mm from each other. These screens form about 150 channels through which the molecules have to travel before entering the parallel

plate region. The divergence of the beam in the direction of propagation of the radiation is estimated to be 1/25 radians. Its contribution to the Doppler broadening results in a half-width ($\Delta\nu_D$) of 2.1 kHz for CH_3OH at 48 GHz. The half-width ($\Delta\nu_H$) due to the Heisenberg broadening is 1.7 kHz at room temperature. The experimental half-width was about 3.0 kHz. The detection system is essentially the same as that described above for the beam-maser spectrometer. The microwave cavity in the BMS is replaced by the parallel cell in the BAS, (the cavity has one single hole for the in- and output of the microwave radiation, while the parallel cell is connected to separate transmitting and receiving horn, but this is not an essential difference). The modulation of the signal is achieved by applying a square-wave Stark voltage (500 V, 1072 Hz) between the plates of the cell. As signal and local oscillators we used two OKI reflex klystrons type 45V10.

The measurements of the $J = 1 \rightarrow 0$ transitions by the BAS were laborous, because the permeability of the channels in the diaphragm decreases quickly during operation due to the sticking of methanol molecules on the inner surfaces of the channels. The effective measuring time was about 10-15 minutes a day. Several days had to be spent to obtain one spectrum. We took special care to keep the frequency sweep region of the spectrum constant during the accumulation time of the CAT. The signal to noise ratio with the CAT was about 20 (80 scans).

III. EXPERIMENTAL RESULTS AND DISCUSSION.

The resonance frequencies ν_o of the four investigated transitions in the absence of hyperfine structure are given in Table I, together with the measured frequencies of the hyperfine components. Recorder tracings with frequency scale for all transitions are shown in Fig.4.

The desired hyperfine coupling constants were derived from the fit of the experimental spectra to the theoretical ones obtained by diagonalizing the Hamiltonian matrix. The matrix elements of the hyperfine Hamiltonian have been calculated in the $|(J_{\gamma\pm} I_4) F_1 I\ F\ M_F\rangle$ representation, which corresponds to the coupling scheme:

$$\bar{J}_{\gamma\pm} + \bar{I}_4 = \bar{F}_1 \ , \quad \bar{I}_1 + \bar{I}_2 + \bar{I}_3 = \bar{I} \ , \quad \bar{F}_1 + \bar{I} = \bar{F} \ ,$$

where γ stands for the quantum numbers $K\tau$. Group theoretical considerations show that for the levels we are dealing with (A-levels), I_1, I_2, and I_3 are coupled to $I = 3/2$ because of the Pauli exclusion principle. The matrix elements are given in the previous Chapter (Eqs.(35) and (42); the index $\pm$ may be dropped if $K = 0$). The relative intensities were calculated from the intensity matrix for low microwave field strength:

$$\bar{\bar{I}} = \bar{\bar{R}}_f^{+} \, \bar{\bar{C}} \, \bar{\bar{R}}_i \ ,$$

where $\bar{\bar{R}}_i$ and $\bar{\bar{R}}_f$ are the matrices diagonalizing the Hamiltonian matrix of the initial and final state of the transition, respectively, and $\bar{\bar{C}}$ is the dipole moment matrix with elements:

$$C_{qr} = \langle q|\mu_E|r\rangle \ .$$

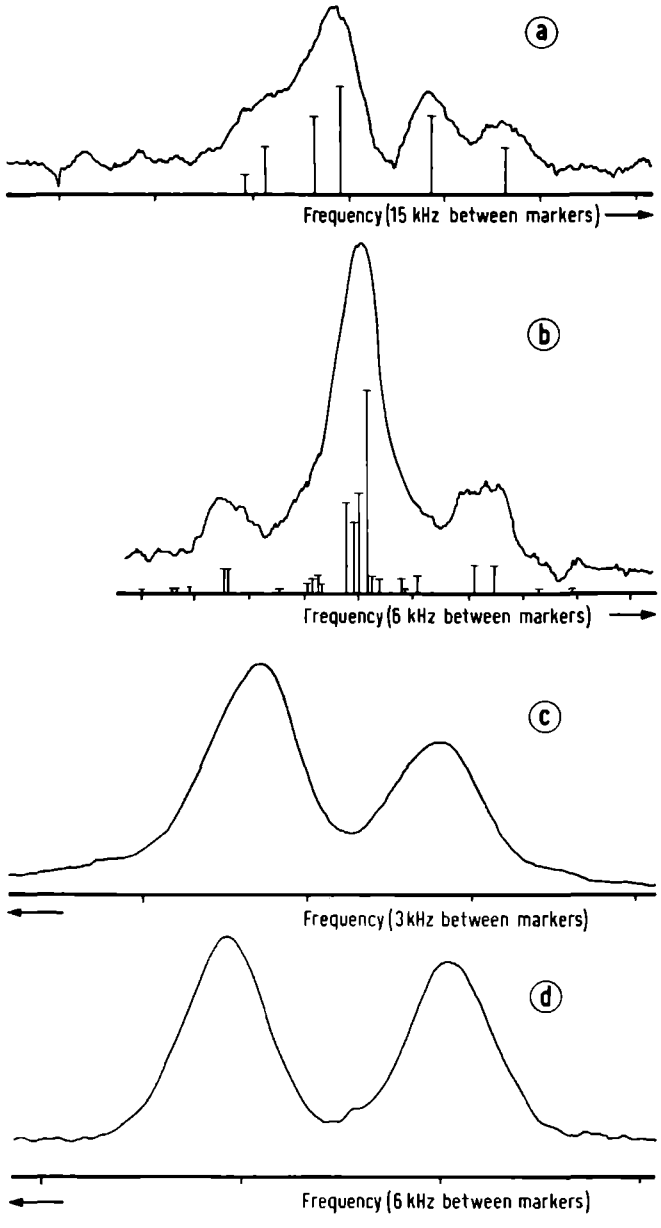

Fig.4. Recordings of the measured transitions: a: (0,0,1)→(1,0,1), b: (2,1,3-)→(2,1,3+), c: (3,1,3-)→(3,1,3+), d: (6,1,3-)→(6,1,3+).

Table I. Measured (column 2) and unsplit line (column 3) frequencies of the CH_3OH rotational transitions (in kHz).

Rotational transition	Hyperfine transition (F_1 ; F) → (F_1' ; F')	Measured frequency	Unsplit line position ν_0
(001) → (101)	(1/2 ;1,2) → (3/2 ; 2)	48 372 467.0 (2)	48 372 455.8 (7)
(213-)→(213+)		2 502 778.45(10)	2 502 778.5 (10)
(313-)→(313+)	(5/2 ; F) → (5/2 ; F)	5 005 318.93(6)	5 005 320.79(20)
	(7/2 ; F) → (7/2 ; F)	5 005 322.18(6)	
(613-)→(613+)	(11/2; F) → (11/2; F)	17 513 337.67(5)	17 513 341.27(20)
	(13/2; F) → (13/2; F)	17 513 344.35(5)	

Herein $|q\rangle$ and $|r\rangle$ is the unperturbed final and initial state of the transition, respectively, and μ_E is the component of the electric dipole moment along the direction of the electric field of strength E. The matrix elements C_{qr} are in the above representation, apart from insignificant constants, equal to (1):

$$C_{JF_1F;J'F_1'F'} = (-)^{J+F_1+F_1'+F+I+I_4} \left[(2F_1+1)(2F_1'+1)(2F+1)(2F'+1)\right]^{\frac{1}{2}} \times$$

$$\times \begin{Bmatrix} F_1 & 1 & F_1' \\ J' & I_4 & J \end{Bmatrix} \begin{Bmatrix} F & 1 & F' \\ F_1' & I & F_1 \end{Bmatrix} .$$

If one of the two states involved in the transition has J equal to zero, the relative intensities of the hyperfine transitions are proportional to 2F+1 (5). If the hyperfine energy matrix is nearly diagonal in the above representation, the hyperfine transitions for a particular rotational transition can be denoted by $(F_1;F) \rightarrow (F_1';F')$. All calculations were done on the IBM 360/50 computer of the University.

The spectrum of the (001) → (101) transition consists of six hyperfine components, only partially resolved. The half-width is about 3 kHz. The coupling constants of the upper level (the lower level with J=0 has no hyperfine structure) are obtained by a curve fitting of the spectrum. The fitting parameters were all four coupling constants $C_{J\gamma}^{(1)}$, $C_{J\gamma}^{(2)}$, $D_{J\gamma}^{(1)}$, and $D_{J\gamma}^{(2)}$ and ν_0. As starting values we took for the spin-spin coupling constants the calculated values, for the spin-rotation constants the value zero, and for ν_0 a reasonable value, easily obtained from the spectrum. The results are given in Table II, column 2. There is a rather good agreement

Table II. Measured and calculated coupling constants (in kHz). The tabulated value of $\Delta C^{(2)}$ is the difference between the $C^{(2)}_{J\gamma\pm}$ constant of the (+) and (-) level of a $\Delta J=0$, $\Delta K=0$ transition.

Coupling constant	(101) level		(213-) level		(313-) level		(613-) level	
	best fit	calc.	best fit	calc.	best fit	calc.	best fit	calc.
$D^{(1)}_{J\gamma}$	-13.8 (9)	-12.7		-9.1		-15.8		-23.5
$D^{(2)}_{J\gamma}$	6.98(90)	6.58		4.7		8.2		-12.2
$C^{(1)}_{J\gamma}$	- 2.4 (10)		- 5.0 (10)					
$C^{(2)}_{J\gamma}$	- 0.6 (10)		- 5.5 (10)					
$\Delta C^{(2)}$					0.93(2)		1.02(1)	

between the calculated and measured values of the spin-spin coupling constants. The calculated values depend on the internuclear distances which means that $D^{(2)}_{J\gamma}$ depends on the internal wave functions $|\tau_K>$, but $D^{(1)}_{J\gamma}$ does not. The angle of internal rotation α is not involved in the mutual distances of the protons in the CH_3-group. The value of $D^{(2)}_{J\gamma}$ however increases only about 3% in the limit of entirely free internal rotation, and decreases in the same amount in the other limit of no internal rotation at all.

The spectra of the J=3 and 6 transitions have an almost identical structure, and are discussed together here. Besides the two strong lines, no other lines were observed in the frequency region of about 200 kHz, in spite of prolonged and careful searching. The calculated spectrum predicts eight strong $\Delta F=0$, $\Delta F_1=0$ transitions and a great number of much weaker transitions of other type: $\Delta F\neq 0$ and/or $\Delta F_1\neq 0$. Consequently the two components in the measured spectra have to be identified with $\Delta F=0$, $\Delta F_1=0$ transitions. These lines are clearly not single lines. This is confirmed by the fact that the ratio of the line widths, obtained with cavities of different lengths, is completely different from the ratio of the lengths of the cavities (6). The calculated value of the spin-spin coupling constants $D^{(1)}_{J\gamma\pm}$ is the same for the upper and for the lower level in our model; the calculated difference between the two values of $D^{(2)}_{J\gamma\pm}$ is less than 0.5% and may be neglected. In order to fit the spectrum four parameters remain to be varied: the spin-rotation constants $C^{(1)}_{J\gamma\pm}$ and $C^{(2)}_{J\gamma\pm}$ of the upper and lower level. The hyperfine matrices of the upper and the lower level are the same except for the values $C^{(1)}_{J\gamma\pm}$ and $C^{(2)}_{J\gamma\pm}$. It is more convenient to ex-

press the spin-rotation constants of the lower level as:

$$c^{(1)}_{JK\tau+} = c^{(1)}_{JK\tau-} - \Delta c^{(1)}$$

$$c^{(2)}_{JK\tau+} = c^{(2)}_{JK\tau-} - \Delta c^{(2)}$$

From Eqs.(37), (49), and (50) of Chap.2 it is clear that $\Delta c^{(1)}$ and $\Delta c^{(2)}$ are independent of J and equal to:

$$\Delta c^{(1)} = \sum_{L=1}^{3} -\mathrm{Re} \langle 3_1 | \{M_L\}^{(2)}_2 | 2_{-1} \rangle = -3\ \mathrm{Re} \langle 3_1 | \{M_1\}^{(2)}_2 | 2_{-1} \rangle ,$$

$$\Delta c^{(2)} = -\ \mathrm{Re} \langle 3_1 | \{M_4\}^{(2)}_2 | 2_{-1} \rangle .$$

We make now the following assumptions:

i) the hyperfine Hamiltonian is almost diagonal in the $|(J_{\gamma\pm} I_4) F_1 I\ F\ M_F\rangle$ representation

ii) $\Delta c^{(1)}$ is small compared to $\Delta c^{(2)}$.

With the assumptions stated above the calculated spectrum splits into two groups of lines with frequency $\nu_1 = \nu_0 - \frac{1}{2}(J+1)\ \Delta c^{(2)}$ and $\nu_2 = \nu_0 + \frac{1}{2}\ J\ \Delta c^{(2)}$, respectively. The first group contains the four transitions with $F_1 = J - \frac{1}{2}$, the second group the four transitions with $F_1 = J + \frac{1}{2}$. The first assumption is fulfilled over a wide range of values of the spin-rotation coupling constants, as can be checked by explicit calculations. For values of the coupling constants outside this range one or more lines (but not all) of each group move to the center of the spectrum indicating a non-negligible contribution of off-diagonal matrix elements. However, a good fit is not possible in this case. The second assumption can-

not be proved in a straightforward way, but the measured spectrum could never be generated if $\Delta C^{(1)}$ is not relatively small. The frequency difference between both groups of lines is:

$$\Delta\nu = \nu_2 - \nu_1 = \tfrac{1}{2}\,(2J+1)\;\Delta C^{(2)} \quad .$$

In order to determine also the sign of $\Delta C^{(2)}$ from the measured spectra it must be known which of the two investigated lines belongs to the $F_1 = J - \frac{1}{2}$ and which to the $F_1 = J + \frac{1}{2}$ transitions. From the relative intensities, tabulated by Townes (7) it follows immediately that the total intensity of the $F_1 = J + \frac{1}{2}$ transitions is larger than that of the $F_1 = J - \frac{1}{2}$ transitions. In the observed spectra (J=3 and 6) the line with the highest frequency has significantly higher intensity and hence can be identified with the $F_1 = J + \frac{1}{2}$ transitions. The observed $\Delta\nu$ values are:

$$\Delta\nu = 3.24(6) \text{ kHz for } J=3 \text{ , and}$$

$$\Delta\nu = 6.68(7) \text{ kHz for } J=6 \text{ .}$$

The resulting $\Delta C^{(2)}$ values are given in Table II. These values do not agree within the quoted experimental error. This is not so surprising because the spectra of the two transitions cannot be put to coincidence by a simple change of the frequency scale; the observed lines are rather broad and not quite symmetrical indicating that the involved transitions in each line are shifted in frequency. This may have its origin in the fact that one or both assumptions made above are not completely fulfilled. The two $\Delta C^{(2)}$ values agree within 10% and hence we write:

$$\Delta C^{(2)} = -\,\mathrm{Re}\,\langle 3_1 | \{M_4\}^{(2)}_2 | 2_{-1} \rangle = 0.98(9) \text{ kHz.}$$

The observed spectra give no information about the other coupling constants.

With the value of $\Delta C^{(2)}$ we calculated the values of ν_0 for J=3 and 6. It is also given in Table I.

The spectrum of the (213-) → (213+) transitions consists of a strong main line and two satellite components originating from $\Delta F \neq 0$ and/or $\Delta F_1 \neq 0$ transitions. To fit this spectrum we made use of the information obtained from the J=3 and 6 transitions: $\Delta C^{(2)}$ = 0.98(9) kHz, and $\Delta C^{(1)} \simeq 0$. Using this information and the calculated values of the spin-spin constants, only the spin-rotation coupling constants of the upper level have to be determined from the fit. The best-fit values are given in Table II. The absence of splitting of the main line into two components, as in the case of J=3 and 6, is readily understood from the fact that for the fitted values of coupling constants, the hyperfine matrices are not diagonal.

IV. CONCLUSIONS.

The spin-rotation coupling constants of the (101) level are:

$$C^{(1)}_{101} = \frac{3}{2} \langle 1_0 | (M_1)_{xx} + (M_1)_{yy} | 1_0 \rangle ,$$

$$C^{(2)}_{101} = \frac{1}{2} \langle 1_0 | (M_4)_{xx} + (M_4)_{yy} | 1_0 \rangle .$$

Consequently only the sum of $\langle 1_0 | (M_L)_{xx} | 1_0 \rangle$ and $\langle 1_0 | (M_L)_{yy} | 1_0 \rangle$ is determined. In fact this is the case for all transitions of CH_3OH. It would be interesting to determine the influence of τ_K upon $\langle \tau_K | (M_L)_{xx} + (M_L)_{yy} | \tau_K \rangle$. However, it is very difficult to extract

the spin-rotation coupling constant from $\Delta J=0$, $\Delta K=0$ transitions, because in this case the coupling constants of the upper and the lower level are almost equal. This causes the strongest hyperfine transitions to coincide. Explicit calculations show that measurements on transitions with $\Delta J\neq 0$ or $\Delta K\neq 0$ would permit the determination of individual coupling constants and their dependence on the internal wavefunction $|\tau_K>$.

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CHAPTER 4

DISCUSSION

I. METHANOL.

The magnetic hyperfine splitting of a rotational level of methanol can be described by four coupling constants: (1) the spin--spin coupling constant of the interactions between the magnetic moments in the frame and the three protons in the top, (2) the spin-spin coupling constants of the interactions between the magnetic moments of the protons in the top alone, (3) the spin-rotation coupling constant of the interaction of the magnetic moment of the proton in the frame with the magnetic fields produced by the internal and the overall rotation, and (4) the spin-rotation coupling constant of the same interaction for the protons in the top. The second interaction vanishes for the levels of E-symmetry. As pointed out in Chap.2, all coupling constants can be described in terms of the components of the coupling tensors $\bar{\bar{D}}_{KL}$, $\bar{\bar{M}}_{K}$, and $\bar{d}_{K}$ of the spin-spin, spin-overall rotation, and the spin-internal rotation interaction, respectively. Now we will discuss the possibility of determining the components of the tensors, rather than the coupling constants from investigated spectra. We restrict ourselves to the spin-rotation interaction, since the spin-spin coupling constants (and tensor components) can be calculated from the known molecular geometry and internal rotation wavefunctions . The agreement with the measured values for the (101) level, for example was quite good and also the same can be expected for the other ro-

tational levels.

The spin-rotation coupling constants are given by Eqs.(37), (38), (49), and (50) of Chap.2 and can be rewritten as:

$$C^{(i)}_{JK\tau(\pm)} = \sum_L \left\{ \tfrac{1}{2} \left[1 - \frac{K^2}{J(J+1)} \right] \langle \tau_K | (M_L)_{xx} + (M_L)_{yy} | \tau_K \rangle \pm \right.$$

$$\pm \tfrac{1}{2} \, \mathrm{Re} \, \langle 3_1 | \{M_L\}^{(2)}_2 | 2_{-1} \rangle \, \delta(K,1) +$$

$$\left. + \frac{K}{J(J+1)} \left[K \langle \tau_K | (M_L)_{zz} | \tau_K \rangle - \tfrac{1}{2} \mathrm{Re} \langle \tau_K | p(d_L)_z + (d_L)_z p | \tau_K \rangle \right] \right\}$$

where the sum runs over L=1,2,3 if i=1 and only over L=4 if i=2. The second term vanishes for E-levels. The contribution of the protons in the top (L =1,2,3) is the same for each proton.

All tensor components are averaged over the internal wavefunctions, and hence only the coupling constants with the same τ and K can be used for the determination of the tensor components. It would be interesting to determine the dependence of the tensor components on the state $|\tau_K\rangle$ of internal rotation. It can be shown by an explicit calculation that the spin-spin coupling constant $D^{(2)}_{JK\tau\pm}$ is nearly independent on the internal wavefunctions, but this does not imply that the same holds for the components of $\overline{\overline{M}}_L$ and probably also for the term $(pd_z + d_z p)$, since it is caused completely by the internal rotation. The contribution, for example, of $\{D_{KL}\}^{(2)}_2$ to the spin-spin coupling constant: $\mathrm{Re}\langle 3_1 | \{D_{KL}\}^{(2)}_2 | 2_{-1} \rangle$ for A-levels with K=1, is very small because of the small dependence on the angle α, while the analogous contribution of $\overline{\overline{M}}_4$ to the spin-rotation coupling constant ($\mathrm{Re}\langle 3_1 | \{M_4\}^{(2)}_2 | 2_{-1} \rangle$) is about 1 kHz (Chap.3) indicating a much larger dependence of the components of $\overline{\overline{M}}_4$ on α.

If sufficient transitions are investigated and the related coupling constants determined, the following quantities might be obtained under optimum conditions:

i) $\langle\tau_K|(M_L)_{xx}+(M_L)_{yy}|\tau_K\rangle$,

ii) $\mathrm{Re}\,\langle 3_1|\{M_L\}^{(2)}_2|2_{-1}\rangle$, and

iii) $K\langle\tau_K|(M_L)_{zz}|\tau_K\rangle - \frac{1}{2}\mathrm{Re}\,\langle\tau_K|p(d_L)_z+(d_L)_z p|\tau_K\rangle$.

The components $(M_L)_{xx}$ and $(M_L)_{yy}$ can never be determined separately, but only as a sum. This is an inherent property of the symmetric top molecules, and CH_3OH is treated as such, which is a very good approximation.

The second term $\mathrm{Re}\langle 3_1|\{M_L\}^{(2)}_2|2_{-1}\rangle$ exists only for A-type levels with K=1, and can be determined only by measuring the spectra of A-type rotational transitions in which one or both involved states is a level with K=1. The term is generated only by the internal rotation and has been already determined (Chap.3).

The most interesting term is, of course, the quantity $\mathrm{Re}\langle\tau_K|p(d_L)_z+(d_L)_z p|\tau_K\rangle$ which describes the spin-internal rotation interaction. Unfortunately this term cannot be determined independently, but only in combination with the term $-2K\langle\tau_K|(M_L)_{zz}|\tau_K\rangle$. If and only if the expectation values of $(pd_z+d_z p)$ and M_{zz} are independent on K (which is open for experimental verification) the two contributions can be separated by measuring the coupling constants of levels with different K-values.

It is clear that many transitions have to be investigated to get more insight in the various coupling tensors and their depen-

dence on the internal rotation. A large number of transitions in the centimeter and millimeter wave region are suitable for this purpose. Recently some of these transitions have been investigated, the E-type transitions (2,1,2)→(2,2,1) and (5,1,2)→(5,2,1) at about 25 GHz by the author (1) and the (2,0,2)→(3,1,1) at about 12 GHz by Gaines (2) with a beam-maser spectrometer and the A-type transition (1,0,1)→(2,0,1) at about 97 GHz by Bicanic (3) with a beam-absorption spectrometer. Unfortunately the resolving power of these spectrometers was insufficient to resolve the hyperfine structure completely (some lines were partially split, others only broadened by the hyperfine interactions). A continued program on the hyperfine structure of methanol will require spectrometers with a resolving power increased by a factor of 5-10. A beam-maser spectrometer with two cavities for the centimeter region or two Fabry-Perot type interferometers for the millimeter region might be very useful (Ramsey patterns).

Another possibility is to investigate partially deuterated species of the methanol molecule (CH_3OD, CD_3OH). The introduced electric quadrupole interaction of the deuterium nucleus is in general an order of magnitude larger than the other hyperfine interactions. It causes a large splitting of the hyperfine spectrum into several lines, which in turn are split by the other hyperfine interactions. Because of the small nuclear g-factor of the D- compared to the H-nucleus (a factor of six), it will be hard to measure the spin-rotation interaction of the deuterium nucleus. Apart from the electric quadrupole interaction, CH_3OD is most suitable to measure the spin-rotation interaction of the protons in the

top, and CD_3OH to measure the spin-rotation interaction of the proton in the frame.

At this moment, no ab-initio calculation of the electronic structure of methanol is available. A continued program on the hyperfine structure might stimulate such calculation.

II. OTHER MOLECULES.

Hydrogen peroxide (H_2O_2) is a favourable molecule for the investigation of hyperfine structure, since it is the most simple internal rotor. The hyperfine splitting of a rotational level can be described in terms of only two coupling constants, namely the spin-spin coupling constant of the two protons and the spin-rotation coupling constant of one proton, which is equal to that of the other. Because of its relative simplicity the molecule is more accessible for ab-initio calculation of the electronic structure (4). However, there are only a few identified transitions in the ground vibrational state known in the easely accessible microwave region.

Both CH_3OH and H_2O_2 are internal rotors with relatively high potential barriers (about 380 cm^{-1}). This implies that the internal motion is more a libration rather than a rotation. It is expected, however, that the influence on the hyperfine interactions, especially the spin-internal rotation interaction, is more pronounced if the internal rotation is nearly free. More information about the internal rotation and hyperfine interactions could be obtained if the investigations are extended to internal rotor molecules with relatively low potential barriers. However, it will be hard to find suitable molecules, since apart from CH_3OH and H_2O_2 most internal

rotor molecules are rather large and intricate. It is expected, that in general the spectra of these molecules will contain clusters of hyperfine transitions because of the presence of many nuclear spins, Resolution of these clusters will require spectrometers of very high resolving power. Moreover, the intensity of the rotational transitions will be rather weak, because of the very large number of rotational levels between which transitions may take place. For a given rotational transition this intensity will be distributed between many allowed hyperfine transitions, leading to very serious sensitivity problems. The prospects of investigating the structure of internal rotor molecules other than methanol and hydrogen peroxide look not very promising.

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In dit proefschrift worden de magnetische hyperfijne interakties in interne rotor molekulen en de metingen verricht aan het methanol molekuul (CH_3OH) beschreven.

Bij het begin van het huidige onderzoek was er geen theorie beschikbaar over de hyperfijne struktuur in interne rotor molekulen. In Hoofdstuk 2 wordt de Hamiltoniaan met inbegrip van hyperfijne interakties afgeleid. De Hamiltoniaan geldt slechts voor molekulen met één interne vrijheidsgraad zoals methanol, maar kan gemakkelijk uitgebreid worden voor interne rotor molekulen met meerdere interne vrijheidsgraden. De magnetische hyperfijne interakties bestaan uit de spin-spin interakties en de spin-rotatie interakties. De spin--spin interaktie is de wisselwerking tussen de magnetische dipool momenten van de kernen onderling. Deze interaktie hangt af van de onderlinge afstanden tussen de kernen en wordt derhalve beïnvloed door de interne rotatie. De spin-rotatie interaktie is het gevolg van de wisselwerking tussen de magnetische dipool momenten van de kernen en het effektieve magnetische veld ter plaatse van de kernen. Dit magnetische veld wordt veroorzaakt, zowel door de rotatie van het molekuul als geheel ("overall" rotatie), als door de interne rotatie. Er zijn dus twee bijdragen tot de spin-rotatie interaktie, namelijk de spin-interne en de spin-"overall" rotatie interaktie. Met behulp van sferische operatortechnieken werden de hyperfijne opsplitsingen van de rotatie niveaus van methanol berekend in termen van hyperfijne koppelingskonstanten. Molekulaire groepentheorie bleek een belangrijk hulpmiddel hierbij. Expliciete uitdrukkingen

konden worden afgeleid voor de koppelingskonstanten van methanol.

De hyperfijne struktuur op de (J,1,3-)→(J,1,3+) rotatie overgangen van methanol voor J = 2, 3 en 6 werd onderzocht met een beam-maser spektrometer en op de (0,0,1)→(1,0,1) overgang met een beam-absorptie spektrometer (Hoofdstuk 3). De beam-maser spektrometer werd gebouwd door Bluyssen (1968) en de beam-absorptie spektrometer door Huiszoon (1966). In beide spektrometers wordt een hoog oplossend vermogen verkregen door gebruik te maken van molekulaire bundels, waardoor de Doppler verbreding van de spektraallijnen sterk wordt gereduceerd. Ter vergroting van de gevoeligheid werden beide spektrometers uitgebreid met een systeem om "time--averaging" technieken te kunnen toepassen. De gemeten spektra werden geïnterpreteerd met behulp van de in Hoofdstuk 2 afgeleide theorie en de relevante koppelingskonstanten konden worden bepaald.

De spin-rotatie koppelingskonstanten kunnen worden uitgedrukt in de komponenten van Cartesische tensoren. In Hoofdstuk 4 worden de mogelijkheden onderzocht om deze tensorkomponenten voor het methanol molekuul te bepalen. Bovendien worden de vooruitzichten besproken om de hyperfijne struktuur te onderzoeken van andere interne rotor molekulen dan methanol.

STELLINGEN

I

De door Kukolich gemeten hyperfijne spektra van $^{15}NH_3$ zijn geïnterpreteerd met foutieve uitdrukkingen voor de matrixelementen van de spin-spin interaktie tussen de waterstofkernen. Het verdient aanbeveling deze spektra opnieuw te analyseren.

S.E. Kukolich, Phys. Rev., **172**, 59 (1968).

II

De bewering van Mariot, dat de nulmatrix een triviale representatie van een groep vormt, is onjuist.

L. Mariot, 'Groupes finis de symmetrie et recherche de solutions de l'équation de Schrödinger', Dunod, Paris, 1959 (p. 10).

III

De mogelijkheid, dat kleine clusters van waterstofmolekulen metallieke eigenschappen hebben, is aan ernstige twijfel onderhevig.

IV

De deoor Rogers en Barrett uitgevoerde berekening van de waarschijnlijkheid, dat interstellaire OH radikalen binnen het $^2\Pi_{3/2}$, $J = 3/2$ Λ-doublet een door elektronen of ionen geïnduceerde overgang maken, is ten dele onjuist.

A.E.E. Rogers en A.H. Barrett, Ap. J., **151**, 163 (1968).

V

Het verband tussen de door Kelsey gemeten sterkten van de 'prebreakdown' stroom en de Rontgenemissie blijkt verschillend te zijn voor verschillende vacuumsystemen. De door de auteur gegeven verklaring met behulp van het Townsend mechanisme is overbodig en onwaarschijnlijk op grond van de afwijkende experimentele omstandigheden.

T. Kelsey, J. Phys. D Appl. Phys., **5**, 569 (1972).

VI

De door Cross *et al.* gegeven waarden voor de totale botsingsdoorsneden bij zuivere multipoolinteracties zijn zeer onnauwkeurig (50%).

R.J. Cross, E.A. Gislason, en D.R. Herschbach, J. Chem. Phys., **45**, 3582 (1966).

VII

Autorijscholen dienen uit didaktisch oogpunt meer dan tot nu toe gebruik te maken van veiligheidsgordels.

VIII

In het voortgezet onderwijs, zeker voor het vak natuurkunde, is geen plaats voor drie verschillende leraarsgraden.

J.E.M. Heuvel

Nijmegen, 14 december 1972